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# MALEIC ANHYDRIDE





# MALEIC ANHYDRIDE

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and

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# PREFACE

In just fifty years maleic anhydride has evolved from a little-known, little-used compound to a truly high-volume chemical. Between 1940 and 1978 its production has increased seventy-fivefold. The fact that more than half of all maleic anhydride produced in the United States is consumed in a single application tends to obscure the great versatility of this intermediate. Because this relatively simple molecule plays a key role in numerous chemical reactions, it finds applications in such diverse areas as adhesives, elastomers, plastics, coatings, fibers, lubricants, fuels, detergents, agricultural chemicals, pharmaceuticals, and surfactants, to name only a few.

The chemistry of the maleic anhydride molecule seems to be uniquely suited to illuminate many facets of organic chemistry. In addition to its important role in functional-group chemistry, study of maleic anhydride lends itself to analysis of such diverse processes as ionic, radical, and cycloaddition reactions. Similarly, polymer chemistry is exemplified in a variety of ways by reactions of maleic anhydride, including its role in charge-transfer, addition, and condensation polymerizations.

Although some aspects of the maleic anhydride molecule are well understood, others need extensive research and elucidation. Further, the development over the last twenty years of new processes utilizing maleic anhydride, such as photochemistry, homopolymerization, and charge-transfer polymerization, suggests that the potential of this intermediate is far from exhausted. Herein, we believe, lies a challenge for chemists and technologists.

The existence of extensive archival, trade, and patent literature and a large market notwithstanding, no comprehensive, hardbound, technical reference work on maleic anhydride has so far been available. This book attempts to correct that situation and provides, for the first time, a single reference source of scientific background information and state-of-the-art technical data on this unique chemical. *Maleic Anhydride* collates the interesting chemistry of maleic anhydride that was until now scattered over 30,000 references, including patents, giving equal emphasis to fundamental and applied chemistry, while at the same time directing the reader's attention to sources for reaction recipes.

In keeping with the authors' intent to furnish chemists, chemical engineers, and others interested in maleic anhydride with an accurate and practical reference source, the book provides not only a review and discussion of key raw materials, production procedures, and the economics of maleic anhydride, but also delves into the multifaceted chemistry and polymerization

reactions of the monomer. Uses, both known and potential, are surveyed and discussed, and attention is also paid to health and safety factors.

It is the authors' hope that the breadth of the material and the thoroughness of presentation will make *Maleic Anhydride* of value to both technologist and scientist as well as to those concerned with the production and marketing of the raw material and its derivatives.

Columbus, Ohio  
1981

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B. M. Culbertson

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# INTRODUCTION

## 1.1. INTRODUCTION

Maleic anhydride (MA)\* was first produced some 150 years ago by dehydration of maleic acid. Today, it is a chemical of considerable commercial importance. Next to acetic and phthalic anhydride, it is the second most important anhydride in commercial use.

From only 4.5 million lbs produced in 1940,<sup>(1,2)</sup> MA has gained impressively, with a production of 341 million lbs in 1978.<sup>(3)</sup> MA has seen some impressive growth periods in the past as is evident in Fig. 1-1. The effect of the oil embargo of 1974 is also evident.<sup>(2)</sup> Japan saw an average 27% increase in MA consumption during the period 1971–1973.<sup>(2,4)</sup>

Table 1.1. Maleic Anhydride Production Capacity<sup>(5)</sup>

Producer	Raw material <sup>a</sup>	Capacity, million lb/year
Amoco Joliet, Illinois	Butane	60
Ashland Chemical Neil, West Virginia	Benzene	60
Denka Houston, Texas	Benzene	50
Koppers Company <sup>b</sup> Cicero, Illinois	By-product from PA	10
Monsanto <sup>d</sup> St. Louis, Missouri		115
Reichhold Chemical <sup>c</sup> Morris, Illinois	Benzene	44
Tenneco Fords, New Jersey	Benzene	26
USS Chemical Neville Island, Pennsylvania	Benzene	80

<sup>a</sup> New EPA regulation requiring 100% control of benzene (no detectable benzene emissions) for new plants may favor butane-based plants in the future (Federal Register, April 18, 1980).  
<sup>b</sup> Koppers shut down a benzene-based facility.<sup>(7)</sup>  
<sup>c</sup> Reichhold closed a benzene-based plant (60 million lb/year) in October 1979.  
<sup>d</sup> Monsanto reportedly uses butane feed stock for about 20% of its capacity. Also, it has announced plans for additional 130 million lb/year capacity of butane-based MA.<sup>(8)</sup> The plant is scheduled to be on stream in early 1983.

\* Sometimes in the literature acronyms MAN and MAH are used. For this work, MA will be used.

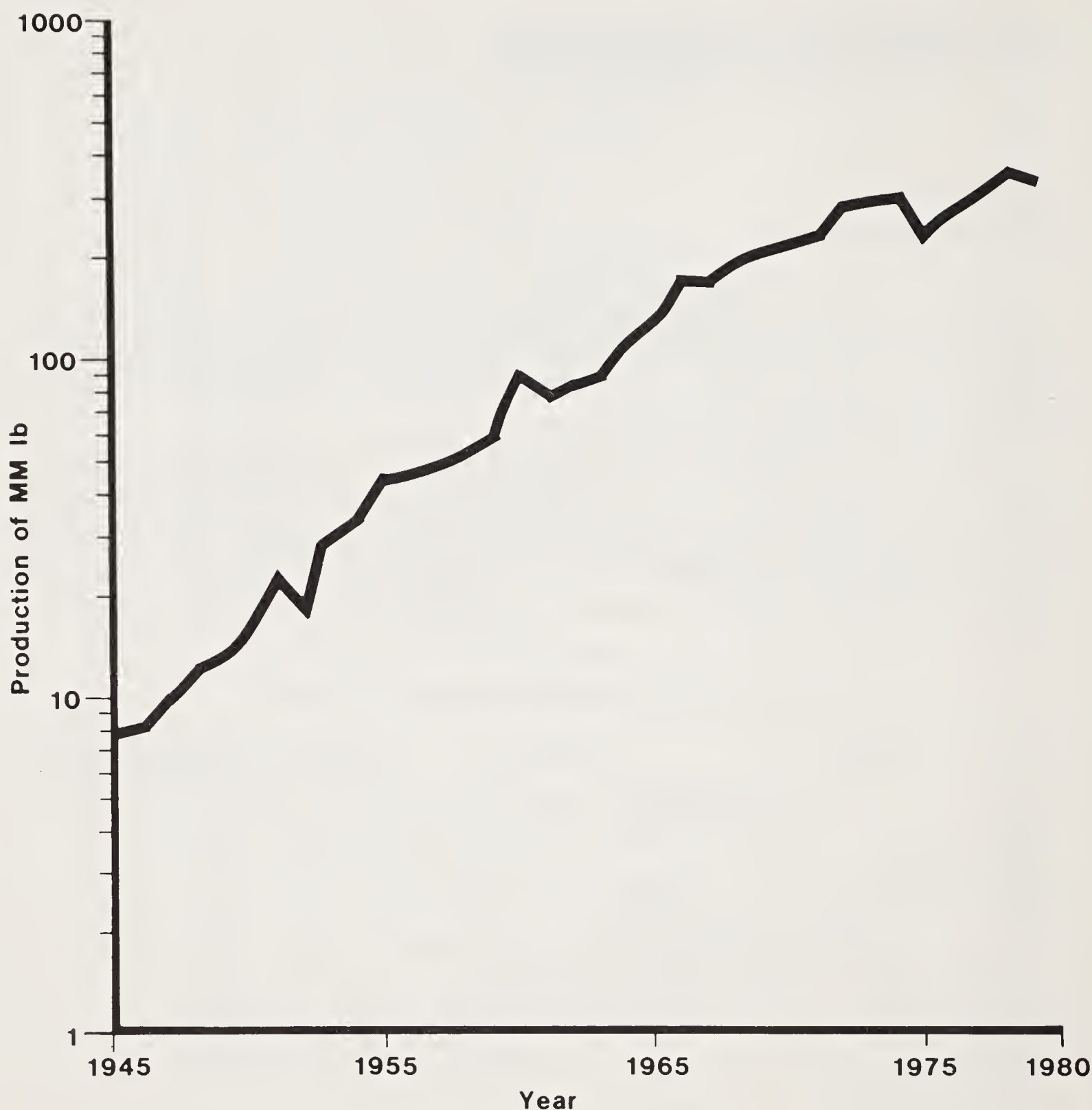


Fig. 1-1. U.S. production of MA.

In the United States there are currently eight major producers of MA. Table 1.1 gives a list of producers along with their location and production capacities; the raw material used by each is also indicated.

## 1.2. PROPERTIES AND STRUCTURE OF MA

Maleic anhydride (MA) is chemically 2,5-furandione,\* or *cis*-butene-dioic anhydride. It is also known by other names such as toxilic anhydride, maleic

\* CAS Registry No. 108-31-6.



Table 1.2. Physical Properties of MA<sup>(9,40,58)</sup>

Crystalline forms	Needles, rhombic
Flash point	Open cup 110°C (230°F) Closed cup 102°C (215°F)
Flammable limits (by volume)	Lower 1.4%, Upper 7.1%
Autoignition temperature	477°C (890°F)
Boiling point at 760 mm Hg	202°C (395°F)
Color	Colorless crystals
Corrosivity	Not corrosive to metals except in the presence of water
Deliquescence	Slight
Density (water = 1.00)	Molten 1.3 g/cm <sup>3</sup> at 70°C. Solid 1.48 g/cm <sup>3</sup>
Heat of combustion	333.9 kcal/mole (332.29 kcal/mole) <sup>(75)</sup>
Heat of evaporation	13.1 kcal/mole
Heat of fusion	3.26 kcal/mole (2.929 kcal/mole) <sup>(62)</sup>
Light sensitivity	None
Melting point (freezing point)	52.8°C (127°F) (However, see Ref. 58)
Odor	Acrid
Solubility in water	Hydrolizes slowly
Specific heat	0.285 (solid), 0.396 (liquid)
Vapor density (air = 1)	3.38
Dipole moment (benzene, 25°C)	3.92–3.95 D <sup>(73)</sup>
Viscosity (absolute)	15 millipoises at 70°C (158°F)
Threshold limit value (OSHA)	0.25 ppm or 1 mg/M <sup>3</sup>

acid anhydride, or malic acid anhydride. It is a white hygroscopic solid and forms orthorhombic crystalline needles. In Table 1.2 physical properties of MA are given.<sup>(9)</sup> Data on vapor pressure of MA are given in Fig. 1-2.<sup>(9,10)</sup> Note that even as a solid it has a significant vapor pressure and this should be kept in mind while handling it.<sup>(11)</sup> Commercially, it is available from producers either as a molten liquid or as briquettes.

Recently, Vykhrest *et al.*<sup>(82)\*</sup> have examined the temperature dependency of the viscosity, electrical conductivity, and density of MA, thus providing data of considerable importance in handling MA.

MA, being an anhydride, is subject to hydrolysis to the acid on storage. Thus, to obtain a pure sample of MA, purification is necessary. It is purified commercially by distillation. In small-scale laboratory-type uses, MA can be purified by sublimation or crystallization. Its solubility in various solvents is given in Table 1.3.<sup>(12)</sup> Chloroform or aromatic solvents such as benzene, toluene, and xylene are adequate as crystallizing solvents. Larger batches may

\* In this reference viscosity and conductivity seem to have been measured at 50°C. This is strange considering the melting point of MA is 53°C (Table 1.2).

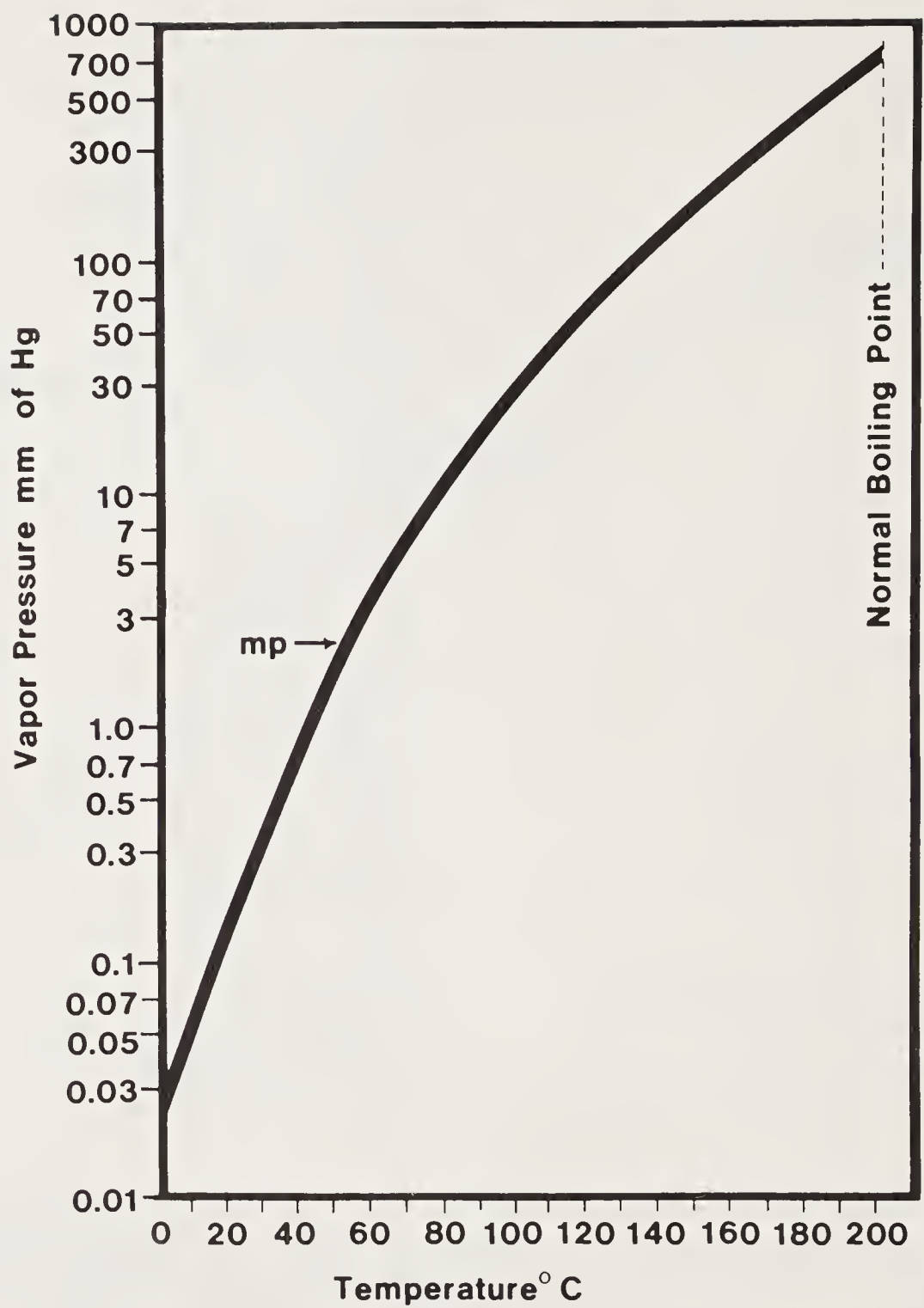


Fig. 1-2. Vapor pressure of solid maleic anhydride. From Reference 12.

Table 1.3. Approximate Solubilities<sup>(12)</sup>

Solvent	Solubility, g per 100-g solvent at 25°C
Benzene	50
Toluene	23.4
<i>o</i> -Xylene	19.4
Carbon tetrachloride	0.60
Chloroform	52.5
Ethyl acetate	112
Alcohol	Very soluble (with ester formation)
Kerosene (b.p. 190–250°C)	0.25
Dioxane	Very soluble
Acetone	227

Table 1.4. Thermodynamic Functions for MA in the Ideal Gas State at 1-atm Pressure

Temperature (K)	Thermodynamic functions, cal/deg.-mole		
	$C_p^\circ$	$(H^\circ-H_0^\circ)/T$	$S^\circ$
298.15	21.24	12.76	71.88
600.0	33.79	20.59	90.19
1000.0	41.02	27.5	110.33

be purified by first dehydrating a sample with a high boiling solvent, e.g., tetrachloroethane, toluene, xylene, etc., thus facilitating to azeotropic removal of water. After dehydration, the solvent may be removed and MA may be distilled under reduced pressure.<sup>(13)</sup> Decomposition of MA in vapor phase is negligible under 350°C.<sup>(78)</sup> Significant decomposition occurs at higher temperatures, the products being acetylene, CO, and CO<sub>2</sub>.<sup>(78,79)</sup>

Thermodynamic functions for MA are reported in Table 1.4.<sup>(61)</sup> The temperature of fusion of 325.65°K and ΔH fusion of 2 929.38 cal/mol have been determined by drop calorimetry.<sup>(62)</sup> ΔG<sub>f</sub><sup>0</sup> for MA in the ideal gas state at 298.15°K has been reported to be −85.5 ± 0.6.<sup>(61)</sup> (Also see Table 1.2.)

Structure of MA

Marsh *et al.*<sup>(14)</sup> have examined the crystal structure of MA using x ray diffraction techniques. In the crystalline state the molecule is essentially planar,

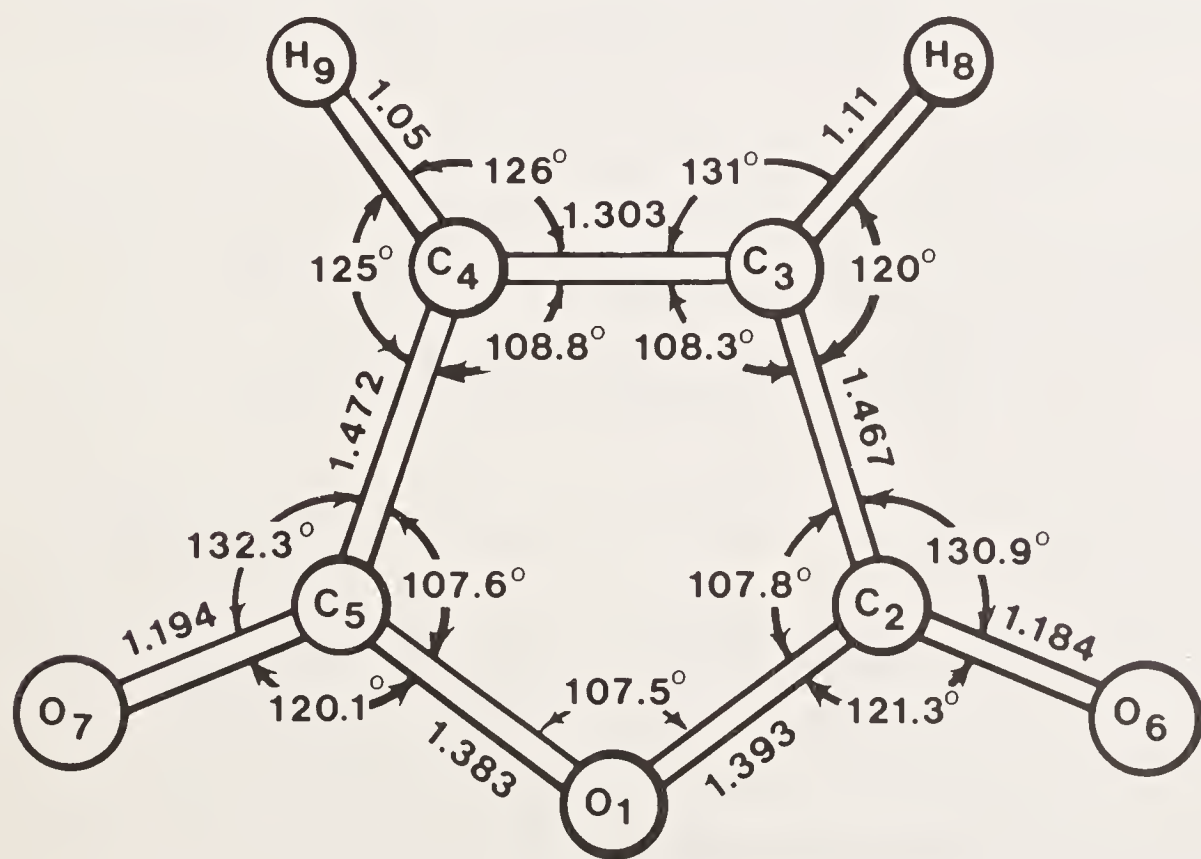


Fig. 1-3. Bond distances and angles in maleic anhydride. After Reference 14. (By permission of International Union of Crystallography, England.)



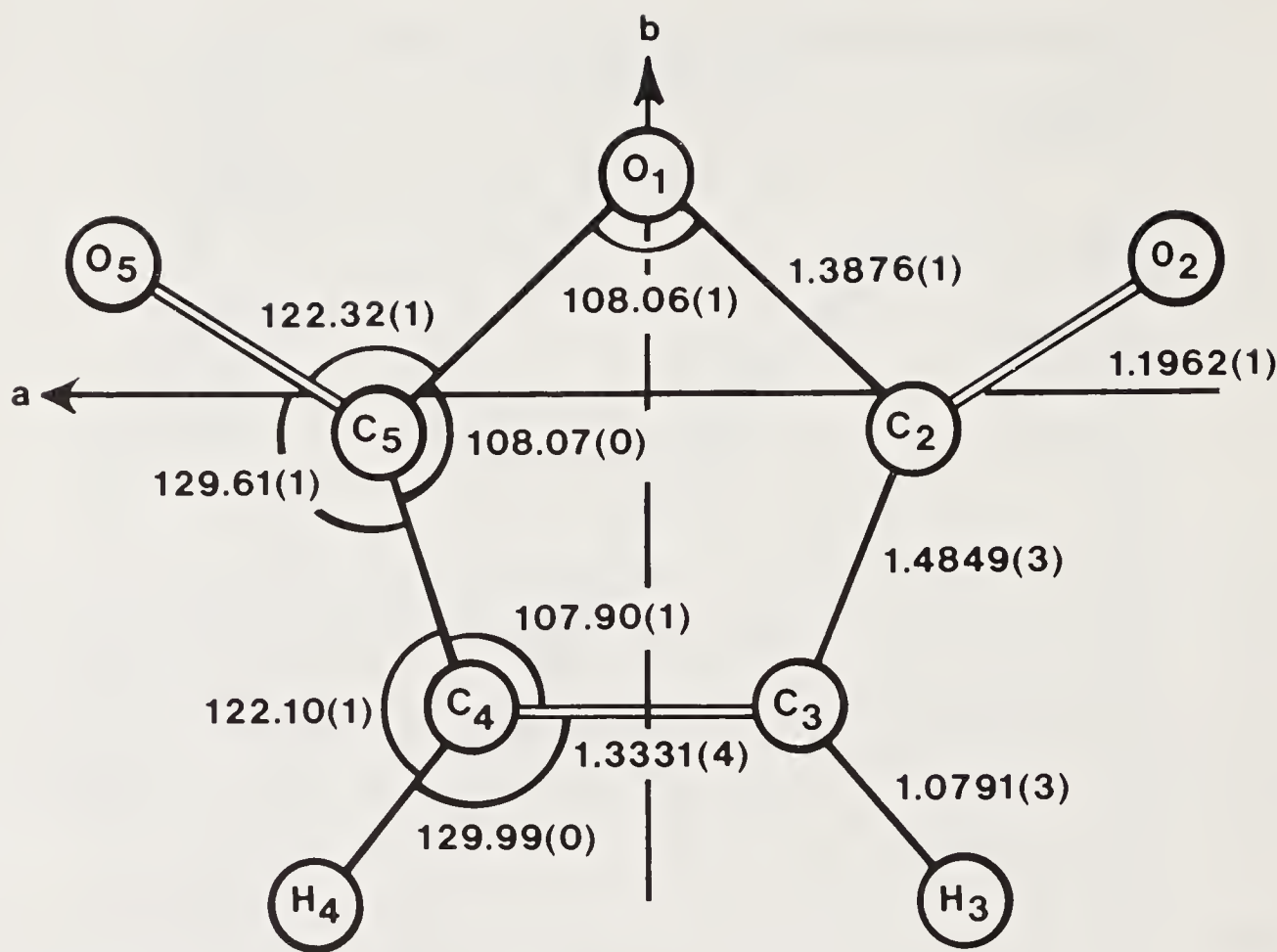


Fig. 1-4. The structure of maleic anhydride. From Reference 15.

with the oxygen atom in the five-membered ring lying 0.03 Å from the plane of the other atoms. The bond distances and bond angles as determined by Marsh *et al.*<sup>(14)</sup> are shown in Fig. 1-3. Other workers studying gas-phase microwave spectra,<sup>(15)</sup> electron diffraction,<sup>(16)</sup> etc. have proposed the molecule to be planar. Recently, Steifvater<sup>(15)</sup> has studied MA using double resonance modulation microwave spectroscopy. The various bond parameters were in good agreement with earlier works. Figure 1-4 represents Steifvater's data.<sup>(15)</sup>

1.3. ANALYSIS

Commercial grade MA is available as molten liquid or as briquettes. Typical specifications are shown in Table 1.5.

Table 1.5. Typical Specifications for MA<sup>a</sup>

% of Maleic anhydride .....	99.5% minimum
Solidification ASTM-D-1493 .....	52.5°C minimum
Molten color ASTM-D-3366 <sup>b</sup> .....	20 maximum on platinum-cobalt scale
Molten color after heating ASTM-D-3366 .....	40 maximum on platinum-cobalt scale
Xylene insolubles <sup>c</sup> .....	clear

<sup>a</sup> Often ash, etc. specification are used for production.  
<sup>b</sup> ASTM-D-3366 Specifies 25.  
<sup>c</sup> This is often included. A solution of 1-g sample in 25 ml of xylene should remain clear. This measures hydrolysis to the acid.

The methods of analysis of pure MA can be taken from specification sheets and are available from producers. However, it is often necessary to determine the amount of MA present in complex mixtures such as reaction products. Following is a summary of methods that have been developed for this purpose.

### 1.3.1. Titrimetric Methods

MA dissolves in water with simultaneous hydrolysis to produce maleic acid. The latter, being a dicarboxylic acid, has two different ionization constants<sup>(58)</sup> at 25°C in water which are

$$pK_1 = 1.83 \quad K_1 = 1.42 \times 10^{-2}$$

$$pK_2 = 6.07 \quad K_2 = 8.57 \times 10^{-7}$$

Thus, maleic acid produced on hydrolysis is usually titrated against an aqueous base (NaOH or KOH) to the two end points at pH = 3.7 and 9.5.<sup>(17)</sup> The ready reactivity of MA with lower alcohols to produce a half-ester, i.e., monoalkyl maleate, may be used in determining MA by titrating to the phenolphthalein end point. The remaining acid moiety of the half-ester is thus titrated as monocarboxylic acid.

The anhydride may also be determined by a potentiometric titration with sodium methylate in methanol.<sup>(18–20)</sup> A combination of both the aqueous method and the anhydrous method gives the amount of acid impurity in MA. For samples containing less than 0.1% acid, a known amount of acid is added to get a clear inflection point in the potentiometric curve.<sup>(19)</sup> Acid impurities can also be determined by potentiometric titration of an acetone solution with a standard solution of tripropylamine or *N*-ethylpiperidine.<sup>(21)</sup> Xylene insolubles, as mentioned earlier, also measure the acid content. In systems where anhydride has to be determined, the anilic acid value<sup>(22)</sup> may be used. Determination of trace quantities could be accomplished using compound formation with dimethylaniline.<sup>(23)</sup> The intense orange-red addition compound (determined colorimetrically) may be used to determine 0.1% MA in some systems.<sup>(24)</sup>

### 1.3.2. Gas-Liquid Chromatography (GLC)

Examples of the quantitative determination of MA using GLC have been reported. In Table 1.6, information concerning stationary phases and solid supports has been given. The key to quantitative determination by this method is calibration. Given that, the method is fast and accurate. In a number of patents involving production, GLC has been used for MA determination in the product stream. In Table 1.6, details about the origin of MA are included. This may help the choice of column since the product distributions are different



Table 1.6. Gas-Liquid Chromatographic Analysis of MA

Stationary phase	Solid support	Remark	References
30% SF-96	Chromosorb W	Naphthalene oxidation	25
15% PEG 4000	Firebrick	Butene oxidation	26
10% PMFS silicon oil	3:1 Chromosorb W-TND-TSM	Naphthalene oxidation	63
Porapak R + SE 30	Chromosorb AW-DMCS	Butene oxidation	64
Porapak R + diisodecyl	Chromosorb AW-DMCS	Butene oxidation	64
10% PFMS-6	Chromosorb W	Naphthalene oxidation	65
22% PEG 500	Celite	Butene oxidation	66 <sup>a</sup>
Porapak Q		Butane oxidation	67

<sup>a</sup> Note: No specific mention of MA, but gave a complete slate based on three different columns.

in various oxidations. In addition, GLC of the esters from MA has been used.<sup>(68,81)</sup>

### 1.3.3. Infrared Spectroscopy

An infrared (IR) spectrum of MA is shown in Fig. 1-5. The most characteristic anhydride bands appear at  $\sim 1780$  and  $\sim 1850\text{ cm}^{-1}$ . The exact position of these bands is slightly dependent on the nature of the sample as well as the solvent used.<sup>(27)</sup> This doublet is usually ascribed to mechanical coupling of carbonyl vibrations. Thus, the high-frequency band is produced by the symmetric (in-phase) stretching mode whereas the low-frequency band is produced by the asymmetric (out-of-phase) mode.<sup>(60)</sup> The  $1780\text{-cm}^{-1}$  band is very strong and can be conveniently used to estimate the amount of MA in a mixture by quantitative IR ( $\pm 1\%$ ). The method is quite useful when solutions are examined by IR. In solutions such as chloroform, benzene, etc., MA has been studied in detail and assignments have been made.<sup>(27,28)</sup> In the presence of other anhydrides,<sup>(29)</sup> particularly polyesters,<sup>(30)</sup> this could be a valuable method. Of course, all standard methods and limitations of quantitative IR determination apply. Infrared spectra of gaseous MA and Raman spectra are also reported.<sup>(27)</sup>

### 1.3.4. Nuclear Magnetic Resonance (NMR)

In the nuclear magnetic resonance spectrum of MA, a characteristic singlet due to equivalent vinyl protons is found at  $\delta = 7.070$  ppm, as shown in Fig. 1-6. This is quite useful also for following reactions of MA both at the anhydride function or at the olefinic function, since in the former case ring opening results in vinyl signals generally at higher fields.  $^{13}\text{C}$  NMR studies for MA have also been reported.<sup>(74)</sup>

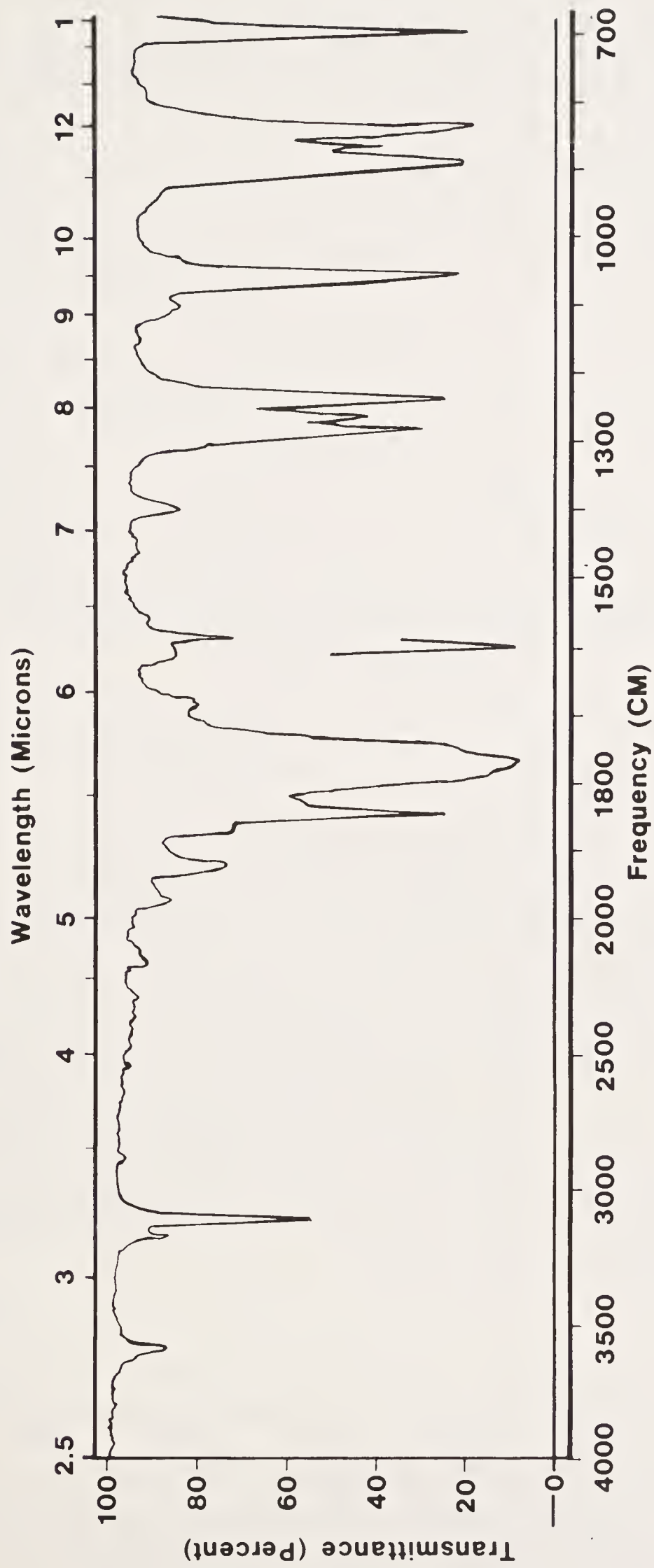


Fig. 1-5. Infrared spectrum of maleic anhydride (KBr pellet).



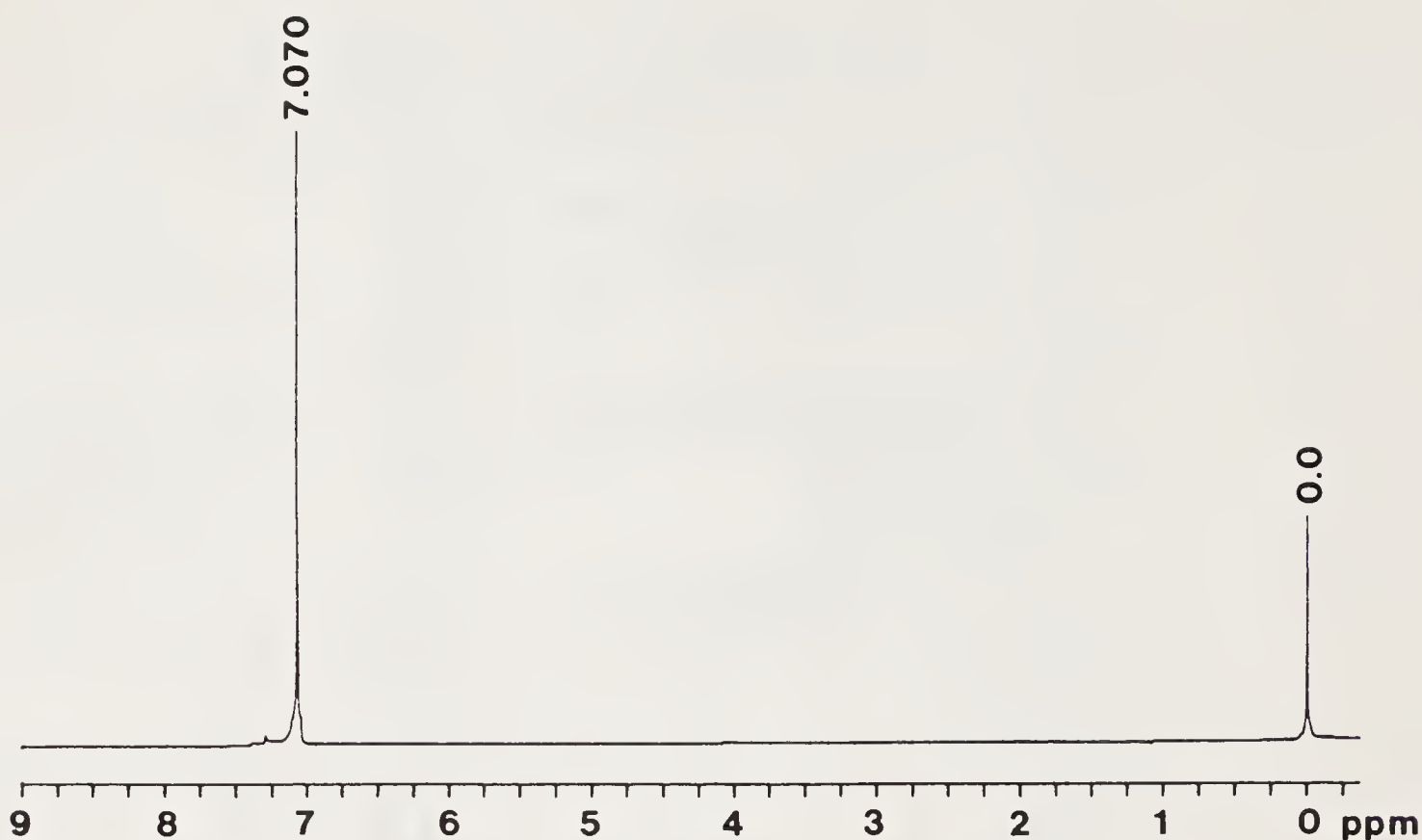


Fig. 1-6. 200-MHz <sup>1</sup>H spectrum of MA. TMS, 0.0006 ppm; MA, 7.070(2) ppm.

### 1.3.5. Miscellaneous

In addition, since MA can be reduced polarographically (half-wave potential  $-0.72 \pm 0.02$  V), the method can also be employed for quantitative determination of MA and its derivatives.<sup>(31,71,72)</sup> This necessitates that the other material present not be reducible or if so, that its half-wave potential be sufficiently different from that of MA.<sup>(31,32)</sup> For MA analysis, nonaqueous solutions have been used. Electronic spectroscopy may also be employed for the analysis of MA. Figures 1-7 and 1-8 represent the UV spectra of MA in solution and vapor phase.<sup>(70)</sup> In addition, thin-layer chromatography by prior derivatization has been employed.<sup>(69)</sup> Due to the Occupational Safety and Health Act, methods of determining lower and lower concentrations of chemicals are required. Such methods may evolve in the near future permitting very precise analysis in various states.

## 1.4. USES

It was estimated that some 341 million lb of MA were produced in 1978 in the United States. This production finds many end uses, the foremost being in the field of polyester resins. In Table 1.7 the breakdown of end uses of MA is shown for the year 1977.

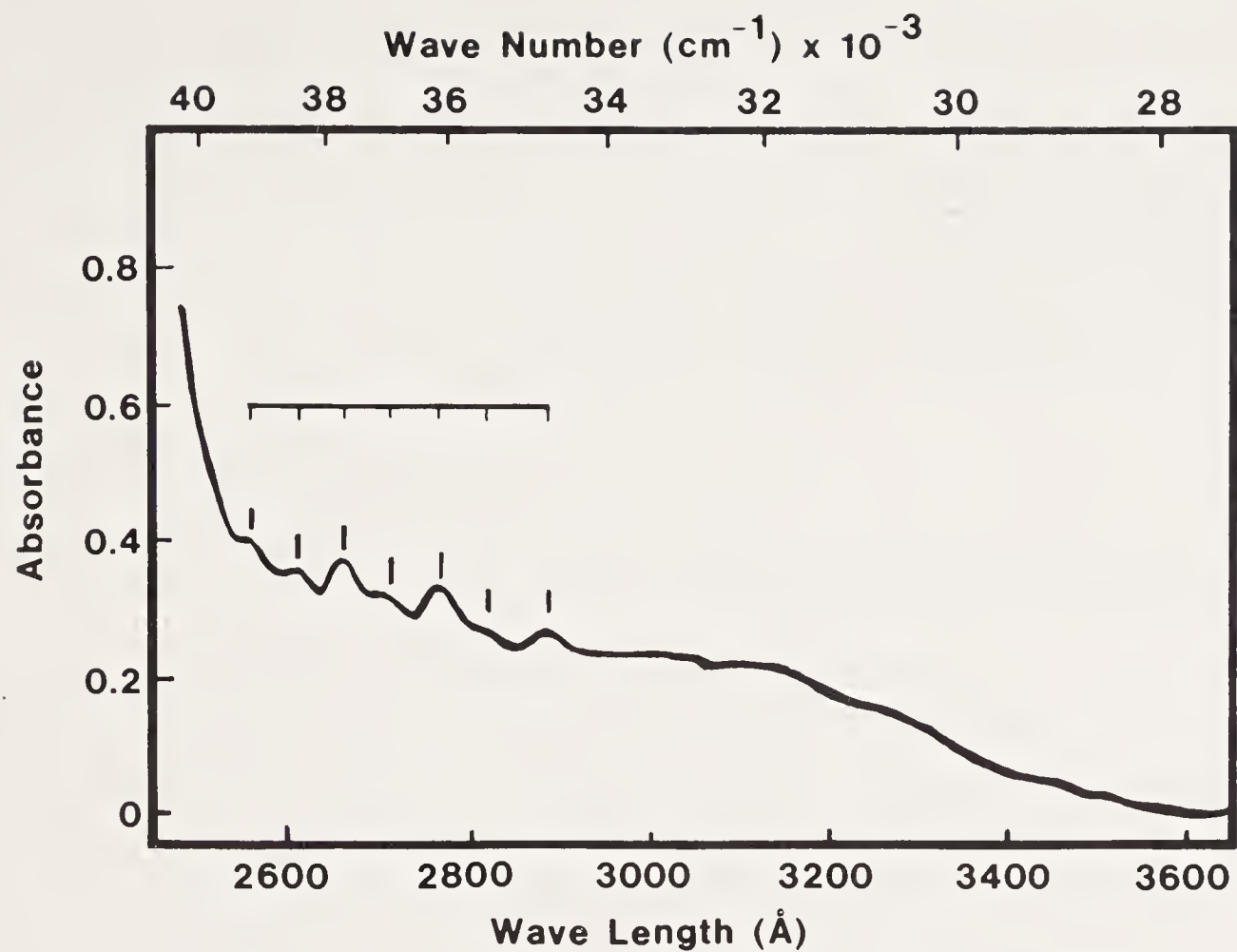


Fig. 1-7. Absorption spectrum of maleic anhydride in 3-methyl-pentane at 300 K (5-cm cell; concentration,  $4 \times 10^{-3} M$ ). From Reference 70.

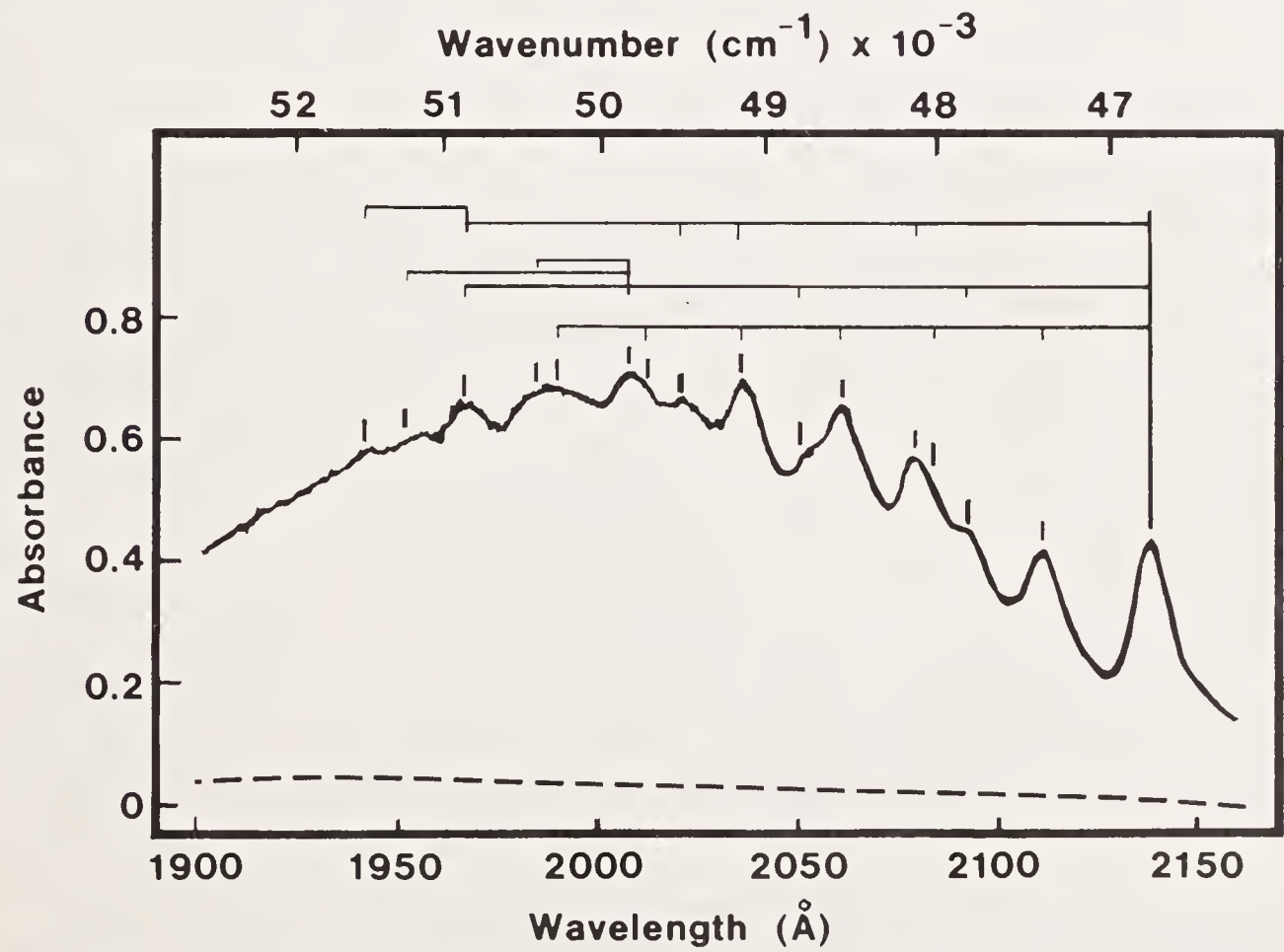


Fig. 1-8. Vapor absorption spectrum of maleic anhydride at 300 K (10-cm cell). The horizontal bars and vertical hash marks denote the vibrational analysis. The dashed line represents the baseline. From Reference 70.

Table 1.7. MA Consumption in the United States<sup>(5)</sup>

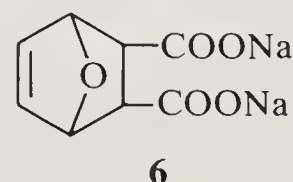
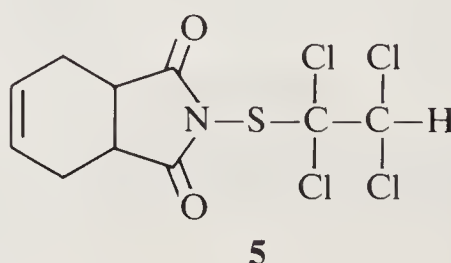
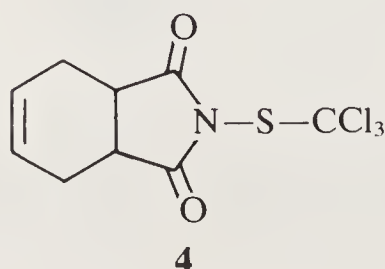
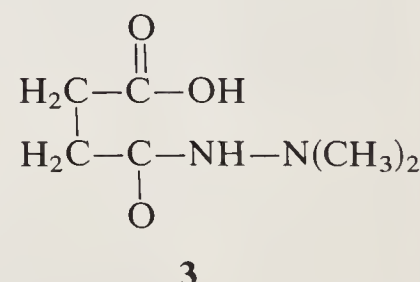
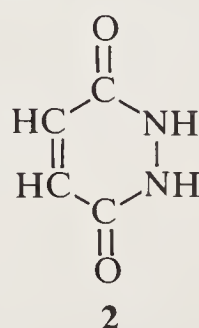
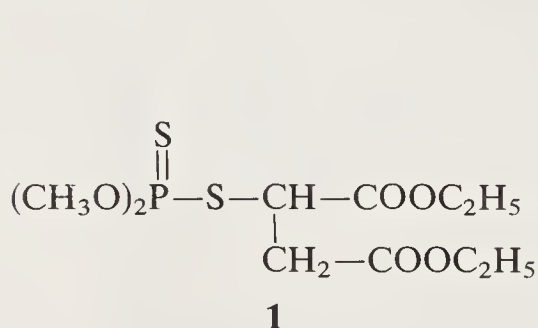
	Percentage of production
Unsaturated polyester resins	52
Agricultural chemicals	9
Fumaric acid	8
Miscellaneous (includes lube oil additives, copolymers, malic acid, chlorendic anhydride, surfactants, plasticizers, alkyd resins, etc.) <sup>(2)</sup>	31

### 1.4.1. Unsaturated Polyesters

Polyester resins consume nearly 52% of MA produced in the United States. These resins find uses in reinforced plastic applications such as automobile, marine craft, building panels, etc. Some resin is also used in nonreinforced applications involving cast furniture parts, synthetic marble, etc.<sup>(2)</sup> According to *Chemical Week*, 1978 was a good year for unsaturated polyester resins—a market which is generally more susceptible to business downturns than most.<sup>(6)</sup> The effect of slowdown in the auto industry began to be felt during the last quarter of 1979.<sup>(76)</sup> The polyester resins business is predicted by some to double by the early 1980s,<sup>(5)</sup> primarily due to growth in automobile uses. (For details on chemistry and applications, see Chapter 12.)

### 1.4.2. Agricultural Chemicals

A number of chemicals contribute to this end use but malathion **1** accounts for half of the MA consumed in the agricultural chemicals.<sup>(33)</sup> Among other popular derivatives of MA are maleic hydrazide, Captan and Difolatan<sup>®</sup>, Endothal and Alar<sup>®</sup>. Malathion **1** is an insecticide; Maleic hydrazide **2** and Alar<sup>®</sup> are herbicides and plant growth regulators; Captan **4** and Difolatan **5**



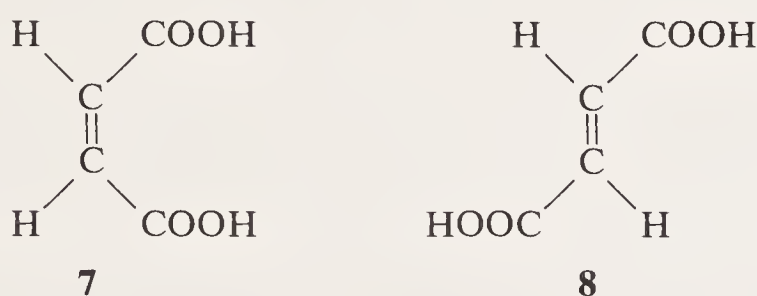


are fungicides. Endothal **6** is an aquatic herbicide also used in defoliation of cotton, alfalfa, potatoes, etc.

Diels–Alder chemistry (see Chapter 4) is widely utilized for preparing agricultural chemicals. The versatility that MA can offer is best summarized in the quote “it is a perfect molecule to make a pesticide because a wide variety of compounds can be made from it and it is environmentally acceptable.”<sup>(33)</sup> A review on biocides based on MA has been published recently.<sup>(34)</sup>

### 1.4.3. Fumaric Acid

Maleic acid **7** which is *cis*-butene-2-dioic acid can be isomerized to its *trans* derivative, namely, fumaric acid **8**, using a variety of techniques.



After the primary recovery of MA during production, the remaining MA is recovered as maleic acid by scrubbing with water. Some of this can be and often is converted to fumaric acid. High-purity fumaric acid for food applications is made from refined MA. The isomerization may be brought about in a number of ways, e.g., thermal,<sup>(35,36)</sup> UV,<sup>(71,83)</sup> or catalytic.<sup>(17)</sup> Aqueous solutions containing 40% maleic acid when heated to 70°C form fumaric acid.<sup>(35)</sup> As a matter of fact, this becomes crucial during MA recovery if fumaric acid is not desired. However, if it is desired commercially, the isomerization is preferably brought about with a catalyst. Numerous catalysts, such as amines,<sup>(37)</sup> HCl,<sup>(38)</sup> thiourea,<sup>(39)</sup> thiocyanates,<sup>(17,45)</sup> 2-mercapto-4-methylthiazole,<sup>(7)</sup> and other thio compounds,<sup>(11,12)</sup> KBrO<sub>3</sub>,<sup>(41)</sup> NH<sub>4</sub>Br + (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>,<sup>(42)</sup> etc. are reported in the literature. Ammonium bromide in conjunction with ammonium persulfate<sup>(42)</sup> bring about instantaneous isomerization at 80–100°C.<sup>(17)</sup> The mechanism of isomerization by acids,<sup>(45)</sup> thiocyanates,<sup>(28)</sup> etc. has been studied.

Nearly 5% of MA produced in 1978 was converted to fumaric acid. The latter is used in paper sizing resins, specialty unsaturated polyesters, as a food acidulant, and flavoring agent. It has been cleared for use as a special dietary and nutritional additive<sup>(43)</sup> and in some indirect applications such as the packaging of food.<sup>(44,53)</sup>

It may be added here that isomerization of other MA derivatives can also be brought about by a variety of reagents.<sup>(40)</sup> This isomerization lends itself to custom designing resins such as unsaturated polyesters by modifying glass-transition temperatures. (See Chapter 12.)

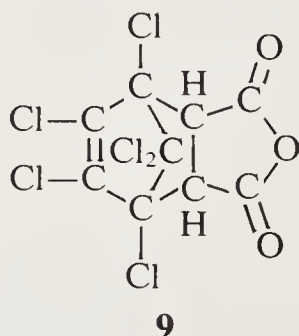
#### 1.4.4. Miscellaneous

In Table 1.7, miscellaneous uses include alkyl resins, which are surface-coating resins used in paints, varnishes, inks, adhesives, etc. This use accounted for a significant share of MA production in the past; however, its contribution has declined considerably recently.

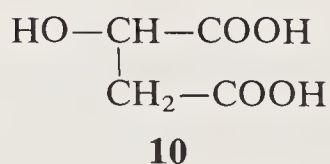
Lube oil additives have increased in importance since better engine performances are required to meet air pollution standards and increased fuel efficiency. End reaction products of MA with olefins, e.g., polyisobutylenesuccinic anhydride, other alkenylsuccinic anhydrides, etc. are used as viscosity index improvers and also as ashless dispersants in the fuels. (See Chapter 5.)

Copolymers of MA with styrene, ethylene, vinyl ethers, allyl acetates and recently  $\alpha$ -olefins are commercially available. These polymers have been suggested for a variety of applications which include adhesives, detergents, textiles, antisoil agents, paper sizing, and time release pharmaceuticals and hair sprays.<sup>(36)</sup> Biologically active organotin polymers made from MA have been found to be useful as antifouling agents for protective coatings in marine applications.<sup>(48)</sup> (See Chapters 9 and 10.)

Chlorendic anhydride **9** is used for making fire-retardant polyester resins. Polyester resins so made are used for insulation of electrical parts, appliance parts, corrosion resistant ductwork, etc. (See Chapter 12.)



MA also finds use as a starting material for malic acid **10** from which it was originally made. Malic acid is used as an acidulant and flavoring agent where it is generally regarded as safe as a miscellaneous or general purpose food additive.<sup>(46)</sup> (See Chapter 3.)



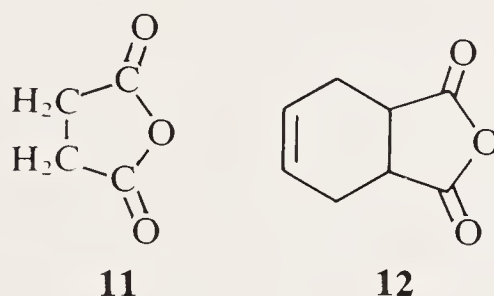
Diesters of maleic acid, which are produced by catalytic esterification of MA, are used as reactive plasticizers for polyvinyl chlorides and polyvinyl acetate resins.<sup>(2)</sup> This is because they can become part of the polymer framework by further polymerization of the olefin function.

Surfactants also form a small but significant outlet for MA. Among the most common are dialkyl sulfosuccinate and monoalkyl sulfosuccinates.<sup>(47)</sup>



Di-2-ethylhexyl sulfosuccinate is a textile wetting agent (see Chapter 3). Carboxymethyloxy succinate (see Chapter 3) and other builders for detergents have been proposed, but their contribution to the MA market is not significant.

Among other uses of MA are preparations of succinic anhydride **11** by hydrogenation and *cis*-1,2,3,6-tetrahydrophthalic anhydride **12** by Diels–Alder (DA) reaction of MA with butadiene. The adduct of MA with isoprene is also available commercially. These DA adducts are used in fire-retardant resins and epoxy hardeners.



MA has been suggested as an additive in numerous other applications which may be worth considering, although some may not be practiced art. These applications include the use of MA as an additive in scale cleaning compositions,<sup>(49)</sup> a stabilizer for *cis*-isoprene rubber,<sup>(50)</sup> imparting heat resistance to cyanoacrylates adhesive,<sup>(51)</sup> and as an additive in fungicide and algicide compositions.<sup>(52)</sup> Dilute maleic acid solution has been studied for cellulose hydrolysis to replace sulfuric acid since the former is less corrosive.<sup>(59)</sup> Cellulose, it may be recalled, forms a large segment of the biomass.

## 1.5. BIOLOGICAL PROPERTIES

The oral LD<sub>50</sub> for rats is 481 mg/kg<sup>(80)</sup> while the subcutaneous LD<sub>50</sub> is 610 mg/kg.<sup>(77,80)</sup> By ingestion, therefore, maleic anhydride in single doses is considered slightly toxic. No reports of cumulative toxic effects in man have been made.<sup>(55)</sup> Recently, the Chemical Industry Institute of Toxicology has sponsored a toxicological study of orally administered MA.<sup>(56)</sup> Hazard in industrial use is essentially that of primary irritation of exposed surfaces.<sup>(9,54,55,57)</sup>

MA is an intense local irritant to body tissue. The irritant effect is exhibited on moist tissues sooner due to MA hydrolysis.<sup>(9)</sup> The dust and vapor are irritating to skin, eyes, nose, throat, and upper respiratory tract. It has a faint acrid odor noticeable at 0.49 ppm.<sup>(11)</sup> Although MA is a solid at ambient temperatures, it does have significant vapor pressure. It is also regarded as a sensitizer of the skin and respiratory tract. Its threshold value is recommended at 0.25 ppm (1 mg/m<sup>3</sup>) in the workplace.<sup>(11)</sup> When left in contact with the skin it can cause severe painful irritation.

Manufacturing Chemists Association data sheet SD-88 gives in detail the fire, explosion, and health hazards. It discusses necessary information for

handling, storage, shipping, etc., which are very pertinent for anyone likely to handle MA and is highly recommended. American Industrial Hygiene Association's Hygienic Guide series is useful as well. For treatment of spills and disposals, manufacturers' brochures and local regulations may be consulted.

## 1.6. EPILOGUE

From the foregoing, it is apparent that MA is a chemical of considerable commercial importance and potential. It has been and can be handled safely as shown by the experience of the chemical industry over the last 50 years. MA, like all chemicals, should be handled and manipulated with due respect and one using it should be aware of all the potential safety considerations. Information on this is available, as indicated earlier.

The variety of uses that MA has demonstrated is due to its versatile chemistry. As a result of its unique functionality, it enters into a variety of reactions in addition to the usual functional group reactions. These aspects are included in Chapters 3–7 of this book.

The main commercial use of MA is as a monomer in unsaturated polyesters. MA's role as a monomer is covered in Chapters 8–12. Aspects such as copolymerization, homopolymerization, and grafting copolymers are included, in addition to the unsaturated polyesters. Utilization of the chemistry of MA discussed in Chapters 3–7 for polymer preparation and modification is also examined.

Production is an important aspect of MA. Considerable activity has recently been brought about by the changing feedstock picture. Chemistry and other aspects of production are discussed in Chapter 2.



# PRODUCTION OF MALEIC ANHYDRIDE

## 2.1. RAW MATERIALS AND HISTORY

The first commercial process for MA production was put into use by National Aniline and Chemical in 1928.\* It used the Weiss and Downs process employing benzene as a raw material.<sup>(1)</sup> In 1930, Monsanto made available MA which was a by-product of their phthalic anhydride manufacture. Petrotex also used their butene-based process in the early 1960s, which was later abandoned in favor of a benzene-based process in 1967. Benzene is still the most popular feed today. Reportedly 90% of world capacity for MA uses benzene.<sup>(2)</sup> Even when benzene was a coal-derived chemical, it was abundant. With the development of the petrochemical industry, benzene was available in larger quantities at lower prices. As a result it became a more attractive raw material. However, the petrochemical industry has in recent years made C<sub>4</sub> hydrocarbons available. There is stoichiometric advantage in using C<sub>4</sub> hydrocarbons over benzene since in the latter two carbons or one-third of the molecule is wasted. Thus, ideally 100 lb of benzene would yield 125.6 lb of MA whereas 100 lb of butane would give 168.9 lb of MA. This intrinsic advantage of C<sub>4</sub>-hydrocarbon-based raw material has shown greater activity for MA production in recent years.

In spite of this, the installation of C<sub>4</sub>-based MA processes has been slow.† The reasons for this are primarily the lack of highly selective catalysts and purification problems associated with this route. It is of interest to note that the raw material price advantage cannot always be the major reason for its choice. This is clearly reflected in recent events. In 1977, Ashland brought into production a 60 million lb/year plant based on benzene, whereas Amoco opted for butane as feedstock in the same year.‡ *n*-Butane and *n*-butenes, however, are gaining favor as the price of benzene climbs steeply<sup>(110)</sup> and

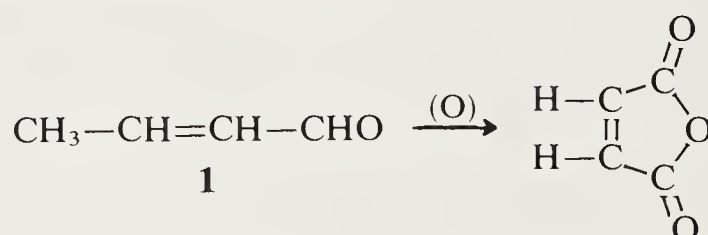
\* However, MA brochure by National Aniline Division of Allied Chemical gives 1933 date for commercial availability of MA. The availability may reflect that of developmental quantities earlier than that date.

† The new EPA regulation requiring 100% control of benzene (no detectable benzene emissions) for new plants may alter the picture to a large extent.<sup>(111)</sup>

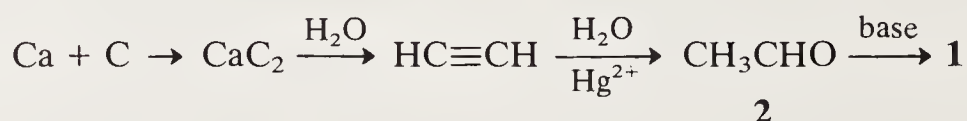
‡ Monsanto has recently announced a plant for 100 million lb to be started in early 1983. The process will utilize butane feedstocks.<sup>(107)</sup> This capacity has been raised up to 130 million lb. (See Chapter 1.)

environmental regulations for benzene take effect.<sup>(111)</sup> DeMaio<sup>(115)</sup> suggests that economics may become important and versatility to handle both benzene and butane on demand may be a viable option. This may be evident in the proposed partial conversion to butane by a number of producers.<sup>(116)</sup>

The choice of raw material can be dictated by other reasons as well. Although there is no evidence of crotonaldehyde being used as a feed commercially, it has been reported that during World War II, I. G. Farbenindustrie made MA by the oxidation of crotonaldehyde **1**. This conclusion was probably based on the patent activity by that company before the war,<sup>(3,4)</sup> although no evidence to this effect was found.<sup>(24)</sup>

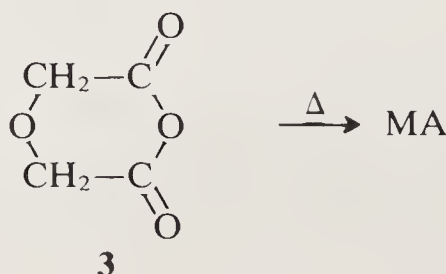


It has been observed<sup>(5)</sup> that acetylene was probably viewed as the raw material of choice for a number of chemicals—including crotonaldehyde **1** by the Germans—because acetylene could be made easily from calcium and carbon.<sup>(6)</sup>



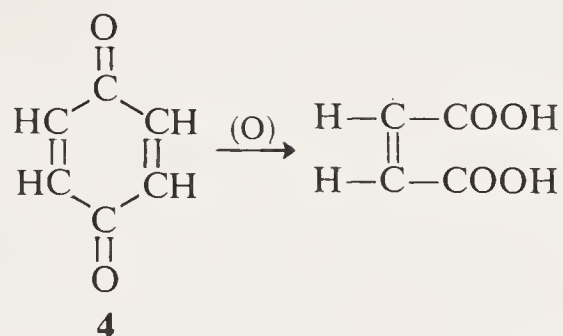
A number of other chemicals have been converted to MA. There is no account of any of them being utilized commercially thus far. Among these are furfural,<sup>(7,14)</sup> mixed olefins,<sup>(8)</sup> cyclopentadiene,<sup>(9)</sup> toluene,<sup>(10-12)</sup> terpenes,<sup>(9,13)</sup> etc. So far, these have been of academic interest due to unfavorable economics and/or low selectivity to MA. Raw material supply and demand pictures are known to change rapidly and particularly so in the recent past. For the present, however, given the present economics and state-of-the-art technology, benzene and C<sub>4</sub> hydrocarbons (*n*-butane in the United States) are the choice of feedstocks. In addition, there is by-product MA produced during phthalic anhydride manufacture.<sup>(1)</sup>

A section such as this would be incomplete if it did not refer to some interesting synthetic routes to MA. Hurd and Glass<sup>(15)</sup> reported that pyrolysis of diglycolic anhydride **3** yielded MA. This method is of more than just historic interest since it provides a built-in potential method of introducing a label in the H, C, or O atoms.





Benzoquinone **4** was first oxidized by Kempf<sup>(16)</sup> in 1905 to maleic acid. Of course, the first preparation of MA was by the dehydrative distillation of malic acid.<sup>(17)</sup> The latter is a predominant acid component of a number of fruits such as apples, bananas, etc.<sup>(18)</sup> (See Chapter 3.)



## 2.2. PRODUCTION TECHNOLOGY

Whether one uses benzene as a starting material or C<sub>4</sub> hydrocarbons, there are some common features in the production technology. These are generally comprised of

1. Reactor design and heat removal
2. Product recovery
3. Purification

There are some basic differences as well and we will see them as we discuss these individual features.

### 2.2.1. Reactor Design and Heat Removal

In MA production, reactor design is of paramount importance because the partial oxidation of hydrocarbons to MA is a highly exothermic reaction and a properly designed reactor is needed to maintain the temperature and hence the reactions under control. An uncontrolled reaction may result in severe reduction of yields and loss of catalyst life.

In a fixed-bed reactor, i.e., a tube packed with catalyst, heat is dissipated by the migration of the temperature gradient<sup>(19)</sup> from the center of the tube to the wall. The size of the gradient is a function of

- tube diameter
- thermal conductivity of the catalyst
- thermal conductivity of the tube
- coolant used

In order to maintain an optimum efficiency of the catalyst, near-isothermal conditions for the reaction are necessary. This means that the longitudinal and transverse temperature gradients should be minimized. This can be

achieved in one of two ways:

- use of small diameter tubes with external cooling
- use of fluidized bed

### 2.2.1.1. *Tubular Reactor*

In almost all MA processes, the small tubular reactor concept is used. The typical reactor contains a bundle of 10–15 thousand tubes, 1 in. in diameter, enclosed by a jacket through which cooling medium circulates. Agitated commercial salt mixtures or circulating heat-transfer fluids are commonly employed.<sup>(20)</sup> The excess heat is thus removed and used in generation of steam for other operations. The literature mentions<sup>(21)</sup> use of ingoing air being used as a cooling medium. Air, so preheated, is allowed to carry the hydrocarbon into the reactor. Space velocity is generally 1 000–4 000 h<sup>-1</sup>.<sup>(40)</sup>

### 2.2.1.2. *Fluidized Bed*

The fluidized beds offer the possibility of controlling the reaction temperature more closely.<sup>(18,22,23)</sup> As a result, this approach has received some attention. Mitsubishi<sup>(24)</sup> in Japan has recently commercialized an MA process based on butenes using a fluidized bed.

In spite of the potential advantages of a fluid bed, all benzene-based processes still rely heavily on the fixed-bed, tubular reactors.<sup>(25)</sup> It is also believed to be the case with the Amoco butane process. The main reason for this overwhelming preference is the difficulty in producing catalysts with low attrition rates.

### 2.2.1.3. *Construction Material*

Since the temperature and by-products are different for processes starting with benzene and C<sub>4</sub> hydrocarbons, the construction materials of various plant equipment may vary. For the benzene-based process carbon steel is considered adequate.<sup>(19,26,27)</sup> On the other hand, in C<sub>4</sub>-based processes, lower acids (acetic, acrylic, crotonic, etc.) are coproduced and hence suitable acid-resistant reactor tubes may be needed. *n*-Butane oxidation is run at higher temperature, and so steel suitable for higher temperature is necessary. It has been suggested<sup>(28)</sup> that a butane-based MA reactor can be easily converted to a benzene-based process but not vice-versa.

## 2.2.2. *Product Recovery*

Besides MA, maleic acid, fumaric acid, carbon monoxide, carbon dioxide, and water are the major by-products of the oxidation of benzene. Benzoquinone, as may be noted, is proposed as an intermediate during MA



formation and small amounts of benzoquinone have been found in the reaction products.<sup>(29,30,31)</sup> In addition, formaldehyde,<sup>(32)</sup> diphenyl,<sup>(32)</sup> phenol,<sup>(33)</sup> and hydroquinone<sup>(33,34)</sup> are reported to be produced in small amounts.

In MA from the C<sub>4</sub>-hydrocarbon process, the nature of by-products is quite different. Among these are the lower monoacids<sup>(35)</sup> (e.g., acetic, acrylic, crotonic), the corresponding aldehydes,<sup>(36)</sup> etc. Some of these are produced in amounts too small to make an economic recovery possible. In either situation (benzene or C<sub>4</sub>), nitrogen, water, and the oxides of carbon are vented to the air after the recovery of products and hydrocarbons. If a significant amount of hydrocarbon is unreacted, it may be recycled if practical. If this is not possible, any of the available emission control technologies, especially for benzene-based processes, may be considered.<sup>(111,112)</sup>

The major difference between various commercial processes is observed in the recovery of maleic anhydride from the effluent stream of the reactor. Commonly employed methods fall into one of the following categories:

- cooling to recover solid MA, m.p. 56°C<sup>(37)</sup> (53°C, see Table 1.2)
- cooling to recover liquid MA
- collecting in a solvent
- collecting in H<sub>2</sub>O or aqueous maleic acid

In practice, as we shall see later, the last category is usually employed as a secondary recovery in processes employing benzene as a feed.<sup>(38)</sup>

The effluent stream contains a low concentration of MA in the gas phase (1.5% by weight). Part of this is recovered as a solid by cooling the effluent as in the Ruhroll process. The Scientific Design (SD) process, on the other hand, collects MA as a molten liquid by cooling the stream above the dew point of water. This prevents formation of any significant concentration of maleic acid produced by hydrolysis which may potentially isomerize to fumaric acid. (See Chapter 1.) The molten MA is collected as such in the Scientific Design process.<sup>(39)</sup> Alternatively, the molten MA can be collected on ceramic supports as claimed by Monsanto.<sup>(40)</sup>

In the solvent-type recovery, MA may be recovered as a solution in dibutyl phthalate, dimethyl phthalate, diphenyl pentachloride, and the like; however, this inert-solvent absorption method is commercially less important.<sup>(41)</sup>

In the aqueous recovery, generally a 40% solution of maleic acid is used in the scrubber. As mentioned earlier, aqueous recovery is a part of most of the processes and is used after a primary collection. The aqueous solution so produced is either used for recovering MA (see below) or may be converted to fumaric acid by thermal isomerization<sup>(18)</sup> (Chapter 1).

### 2.2.3. Purification

Where water is a part of the recovery system as in maleic acid solution, water is removed by azeotropic distillation. Appropriate care is taken to

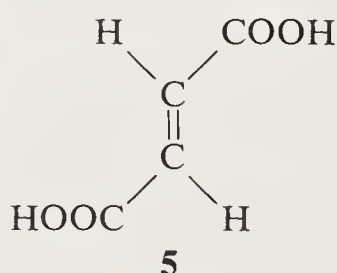
prevent significant isomerization. Commonly employed solvents for azeotropic removal of water are xylene<sup>(42,43)</sup> or *o*-dichlorobenzene.<sup>(44)</sup> Octane,<sup>(45)</sup> diisobutyl ketone,<sup>(46)</sup> etc. have also been claimed in the patent literature. Thin-film evaporation technology has also been employed.<sup>(99)</sup>

The MA so produced and that from the primary recovery are combined at this stage and purified by distillation. The distillation can be performed on the crude product as such or in the presence of an additive. The purpose is to obtain a low-color and color-stable MA (see specifications, Chapter 1). The reagent added prior to or during the distillation serves to interact with and remove potential color bodies. Among a number of reagents claimed for this step are benzoquinone,<sup>(47)</sup>  $P_2O_5$ ,  $MgCl_2$ ,<sup>(48)</sup>  $CaO$ ,<sup>(49)</sup>  $NH_4H_2PO_4$ ,<sup>(49)</sup> alkali sulfate and persulfate,<sup>(44,50)</sup>  $(NH_4)_2SO_4$ ,<sup>(51)</sup>  $BaCl_2$ ,<sup>(52)</sup> sodium borate,<sup>(53)</sup> sulfonic acids,<sup>(54)</sup>  $ZnCl_2$ ,  $NiCl_2$ ,  $FeCl_3$ ,<sup>(55)</sup> dimethylbenzophenone,<sup>(56)</sup> tolualdehyde,<sup>(57)</sup> organic sulfides,<sup>(58)</sup> etc.

The color stability of the distilled MA is claimed to be improved also by an addition of 0.01% EDTA.<sup>(59)</sup>

#### 2.2.4. By-Products

An aqueous maleic acid solution on heating above 70°C yields fumaric acid by isomerization.<sup>(18)</sup> This can be taken advantage of to produce fumaric acid. (See Chapter 1.) However, the demand for **5** is not high. As a result, where aqueous recovery is necessary (second stage in most benzene processes or in all  $C_4$  processes), extreme care is taken to prevent excessive heat treatment of maleic acid solutions.



### 2.3. MA PROCESSES

Before going to the mechanistic aspects of the reaction of either benzene or  $C_4$  hydrocarbon, let us briefly examine some processes commercially utilized for the production of MA. A number of companies use their own proprietary processes and the details of these are not available. However, some processes are known from literature and/or are available for licensing. As a result, a general outline of the process is known. This is the case with both benzene and  $C_4$ -hydrocarbon raw materials. Generally, yields from benzene oxidation are in the range of 60–72% of theory.  $C_4$  oxidation gives 27–40% yields;



however, yields in excess of 48% have been claimed.<sup>(41,99,109,110)</sup> Recently, butadiene has been claimed to give a 75% yield of MA.<sup>(113)</sup> Some of the processes are briefly discussed below.

In the reactor, air containing benzene below its explosive limits is introduced at 350–450°C at slightly above atmospheric pressure (18–35 psi). The pressure is necessary to overcome the resistance in the system. Working with benzene or C<sub>4</sub> hydrocarbons, the following explosive limits are observed<sup>(24,60)</sup>:

Benzene	1.4–7.1 mole % in air	1-Butene	1.6–9.3 mole % in air
1,3-Butadiene	2.0–11.5	2-Butene	1.8–9.7
<i>n</i> -Butane	1.9–8.5		

When a fluidized catalyst bed is used, concentration in the explosive range can be used.<sup>(22,23)</sup>

### 2.3.1. Benzene-Based Processes

#### 2.3.1.1. *Scientific Design (SD) Process*<sup>(61)</sup>

It is believed that approximately  $\frac{2}{3}$  of all MA plants use the benzene-based process. The first plant to use this process was in France in 1957. The overall process is represented by the flow diagram in Fig. 2-1. The benzene–air (1.3%) mixture is preheated and passed over a catalyst in a cooled, multitubular reactor. The catalyst is vanadium oxide based specially developed by SD. The hot effluent from the reactor passes through the preheater to heat the ingoing reactants. A partially cooled effluent is passed through a series of three condenser separators. In the third condenser, which is maintained at slightly above the melting point of crude MA (53°C), the product is recovered as a molten liquid. This avoids plugging due to solidification of MA. The residual MA in the stream is scrubbed with an aqueous maleic acid solution. Normally, the solution is brought to 40% of acid. Practically all remaining MA is recovered by this aqueous scrubbing.

The aqueous maleic acid is freed from water by an azeotropic distillation with *o*-xylene and converted to MA in the process. The process is designed to minimize thermal isomerization of maleic acid to fumaric acid. MA from this step and from direct condensation are combined and refined by distillation.

#### 2.3.1.2. *Ruhrol–Lurgi Process*

The flow diagram is shown in Fig. 2-2. In the process,<sup>(62)</sup> a mixture of benzene and preheated air passes through a multitube reactor cooled by a circulating salt bath. A fixed bed of granular catalyst is used. The conversion of benzene is not complete.

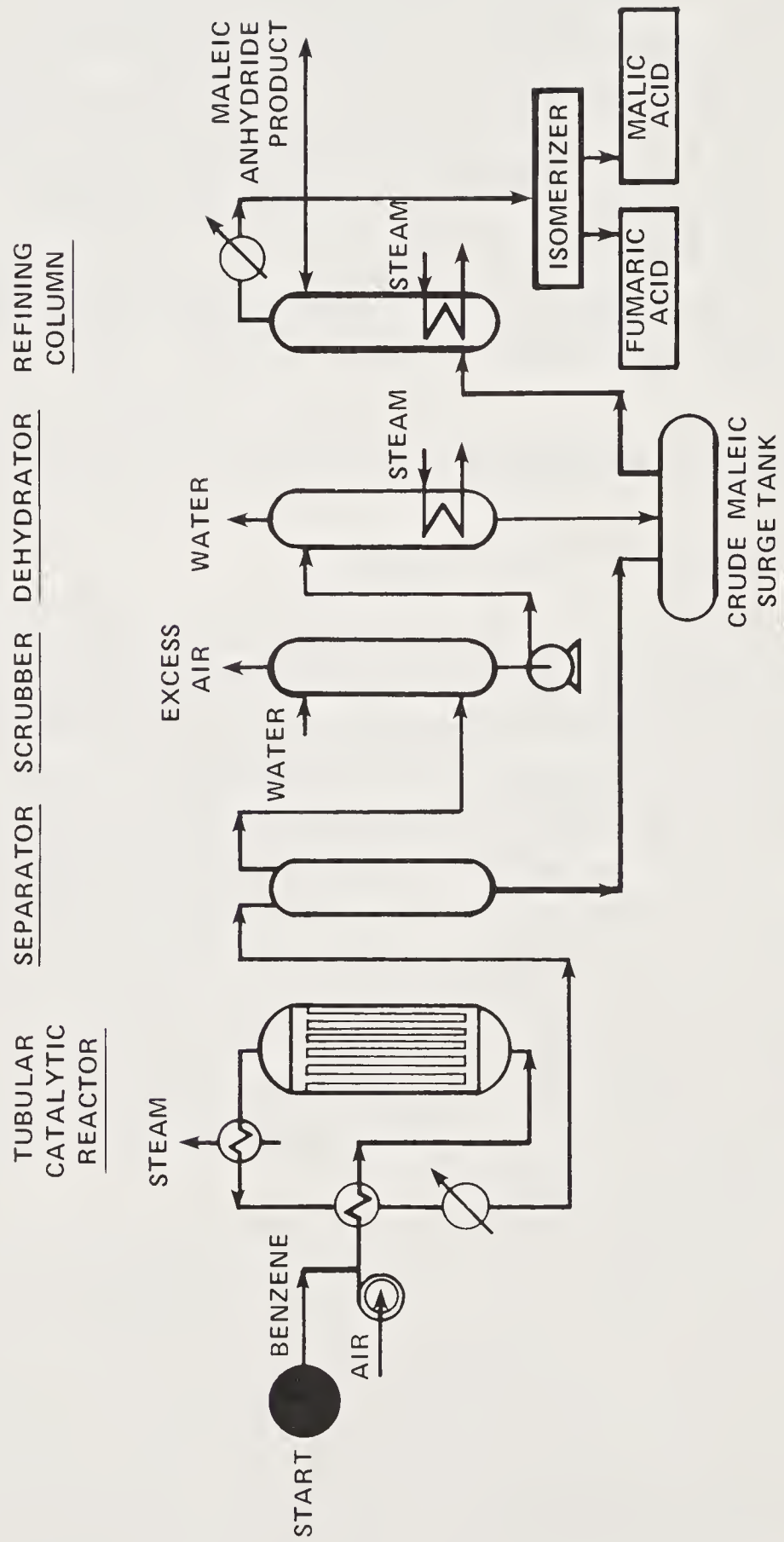


Fig. 2-1. Scientific design process. From Reference 61.

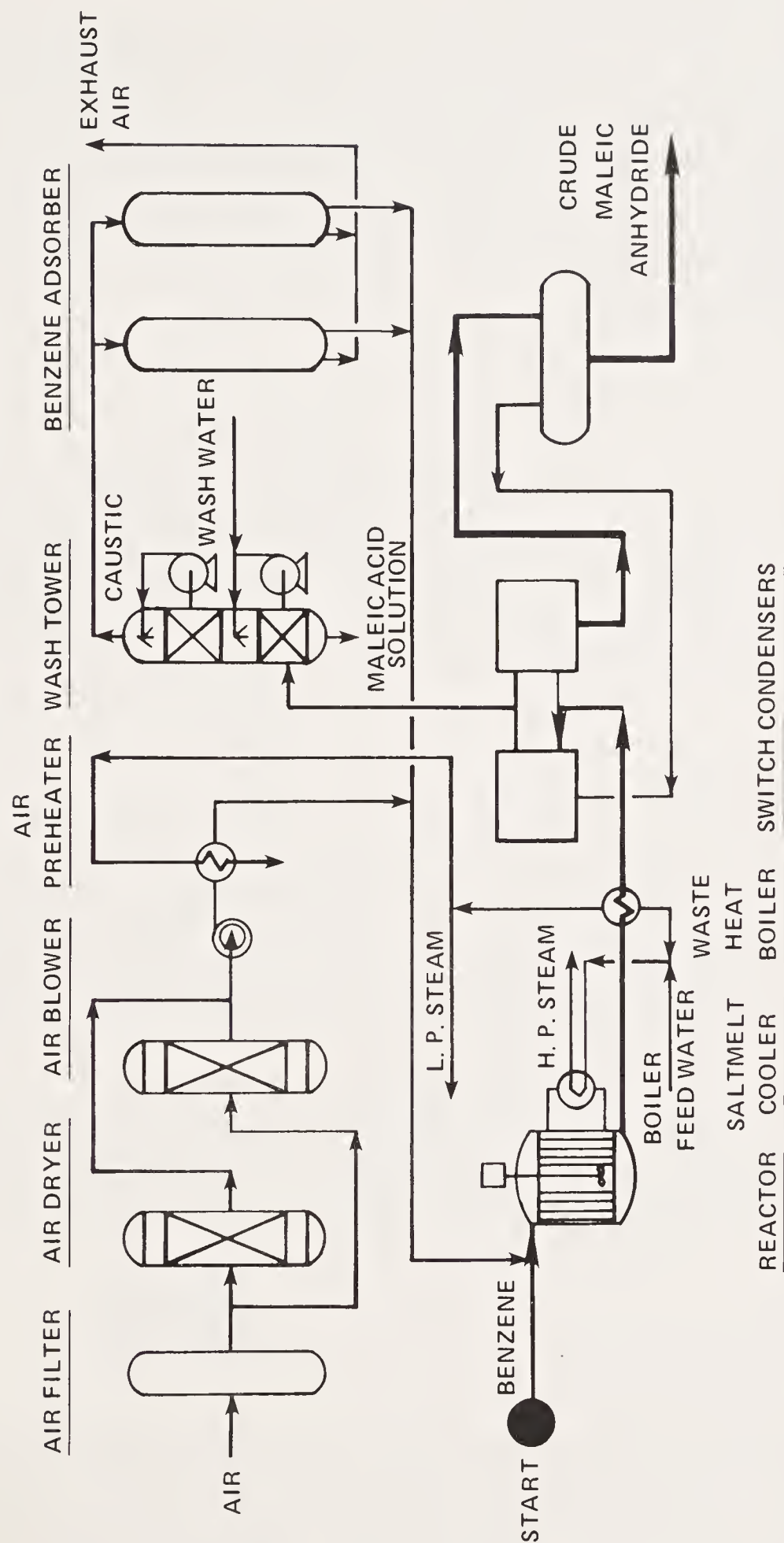


Fig. 2-2. Ruhrol-Lurgi process. From Reference 62.



The MA is recovered as a solid + liquid in switch condensers. After the condensers are switched, MA is melted for refining by batch distillation. Recovery is 90%, the remaining 10% MA being removed in a two-stage scrubber with water and dilute alkali.

Unconverted benzene is recovered from the exhaust gases in an activated carbon unit. The benzene so obtained is returned to the feedstock. These recovery steps, all combined, make the exhaust gases dust and odor free.

The MA recovered in the scrubber is converted to fumaric acid, producing 8 kg of fumaric acid per 76 kg of MA. This makes the process somewhat dependent on demand balance between MA and fumaric acid. The overall yields are claimed to be good.

### 2.3.1.3. *Ruhrol-Bayer Process*

This process<sup>(63)</sup> is a modification of the basic Ruhrol process. The recovery system is similar to SD, i.e., part of the effluent is recovered as molten MA and part as an aqueous maleic acid solution. The latter is dehydrated by azeotropic distillation with xylenes (Fig. 2-3). Benzene in the exhaust gases is removed in absorbers, making it odor free.

### 2.3.1.4. *SAVA Process*

In this process,<sup>(65)</sup> an air-benzene mixture (3-wt. % benzene) is fed to a tubular reactor (see Fig. 2-4). The tubes are loaded with a vanadium complex catalyst on extruded cylinders or spheres of alumina. Molten salt bath is used to maintain the temperature of 355–375°C. The recovery system is quite similar to the SD process. Very high yields and long catalyst life have been claimed.

In addition to these, there are processes such as the Alusuisse/UCB process,<sup>(64)</sup> developed by the two firms with claims of higher yields (86% overall). Other variations of benzene oxidation utilized by various firms are similar to the SD process, the main difference being in the recovery and purification steps.

## 2.3.2. *C<sub>4</sub>-Based Processes*

The potential stoichiometric advantage of producing MA from saturated and unsaturated C<sub>4</sub> hydrocarbon has long been of interest to the industry, even though the oxidations are less selective. Either *n*-butane or a mixture of butene-1 and butene-2 are used as a feed. The latter is derived from refinery hydrocarbon cracker after the removal of chemically useful butadiene and isobutylene. A number of companies have developed processes for MA



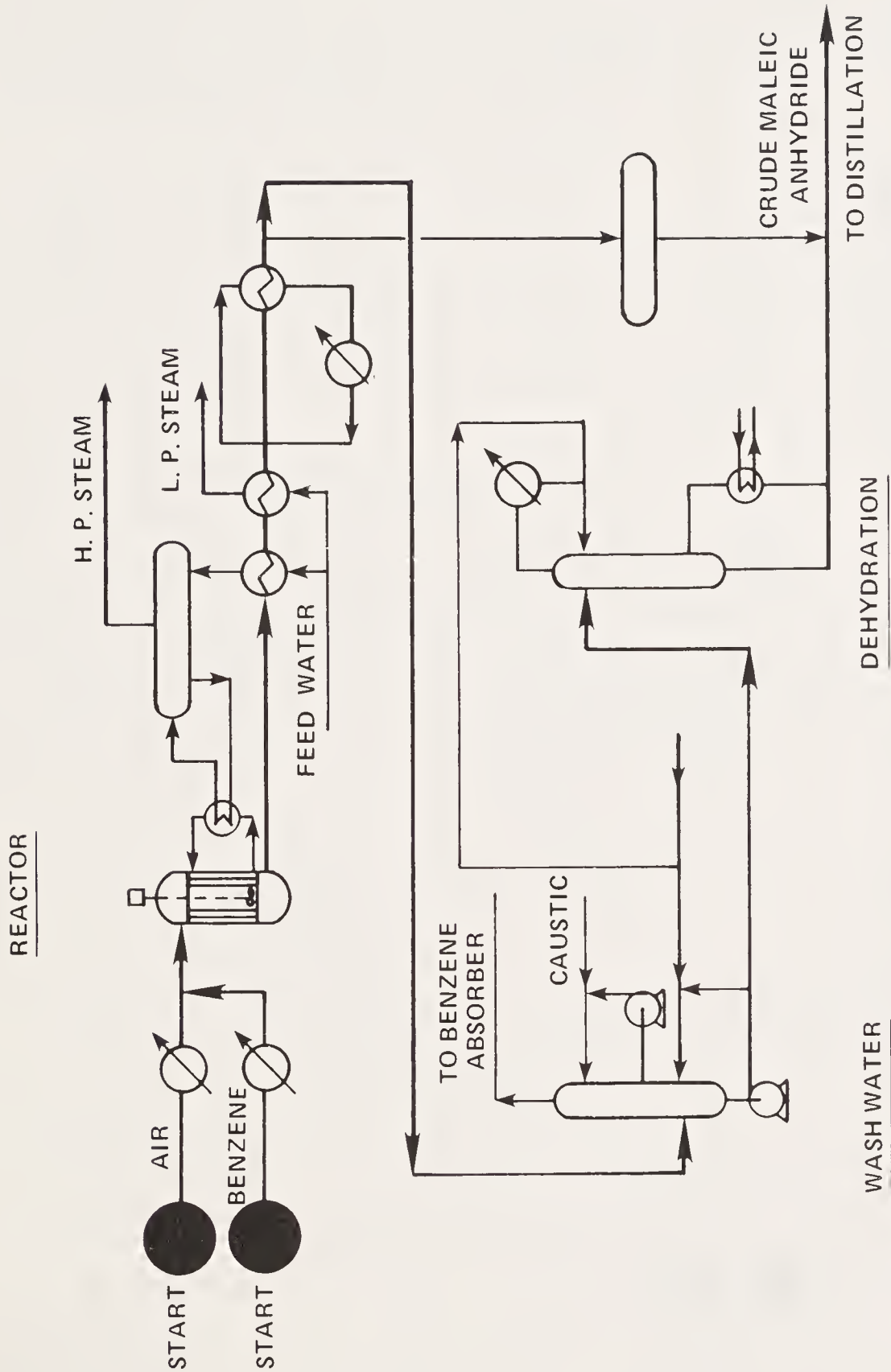


Fig. 2-3. Ruhrol-Bayer process. From Reference 63.

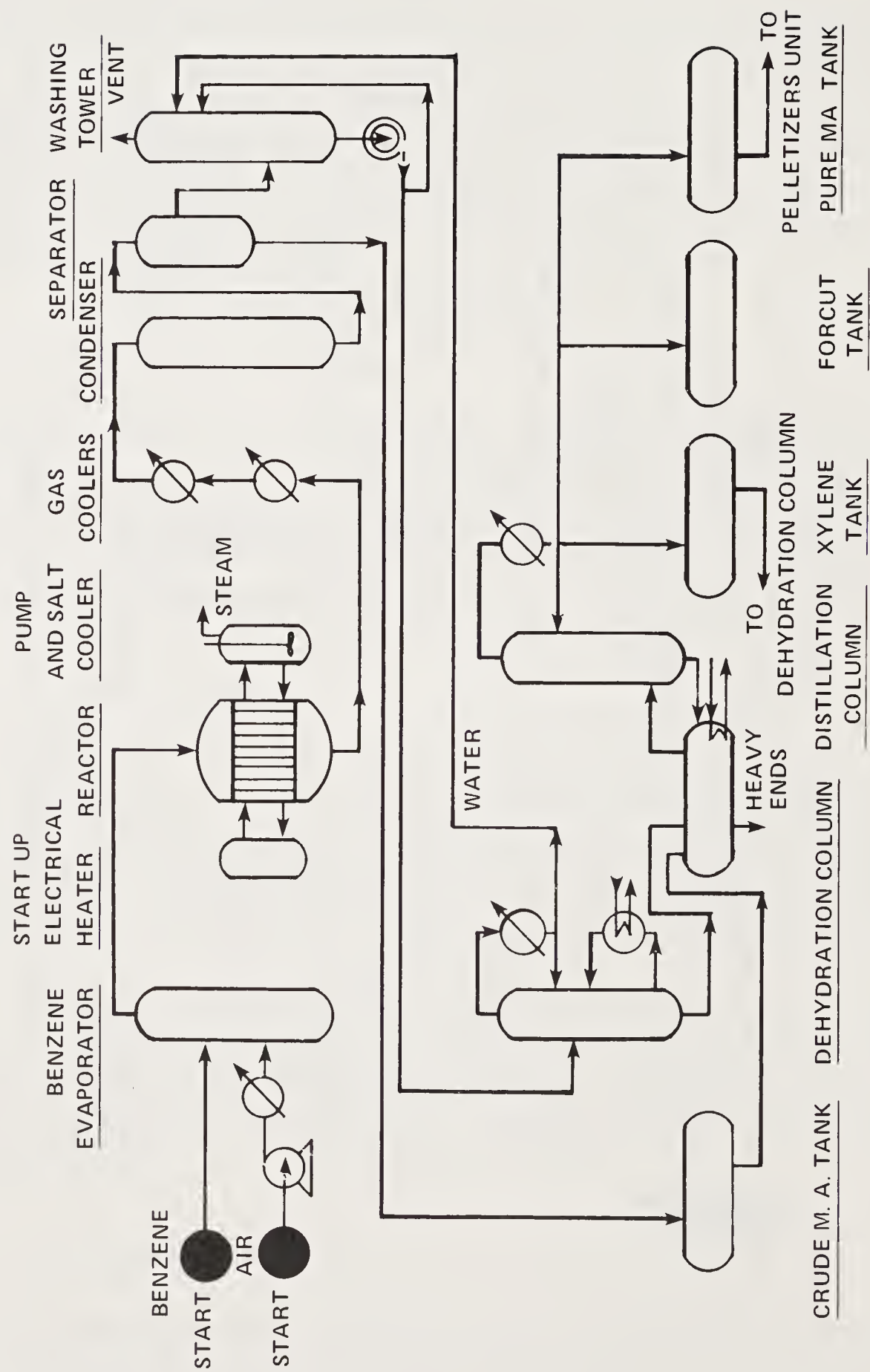


Fig. 2-4. SAVA process. From Reference 65.

manufacture by this route such as Petrotex (Denka), Amoco, BASF, Mitsubishi, Monsanto, Chem-Systems, and Chevron.

It appears that in a  $C_4$ -based process, MA is not recovered directly but as aqueous maleic acid. The reasons are:

- Lower feed/air ratio makes the MA concentration in exhaust gases uneconomical to recover directly.<sup>(66)</sup>
- The process produces more water than the benzene route both due to the stoichiometry and poorer selectivity.

### 2.3.2.1. Mitsubishi Process

This process<sup>(67)</sup> (see Fig. 2-5) came into use in 1970. It uses a  $C_4$  fraction as a feed and hence can use *n*-butane or *n*-butenes containing butadiene and isobutylene. This allows for selection of best operating conditions based on economic consideration. There are two unique features to the process:

- a fluidized catalyst
- concentration and dehydration of maleic acid in a short time

These features are claimed to give this process a number of important advantages.<sup>(66,68)</sup> Cheap raw material produced from large-scale naphtha cracker can be used. Furthermore, the hydrocarbon/air ratio can be higher than the explosive limits since a fluidized bed is used. Since the latter operates at near isothermal conditions, catalyst life is increased.

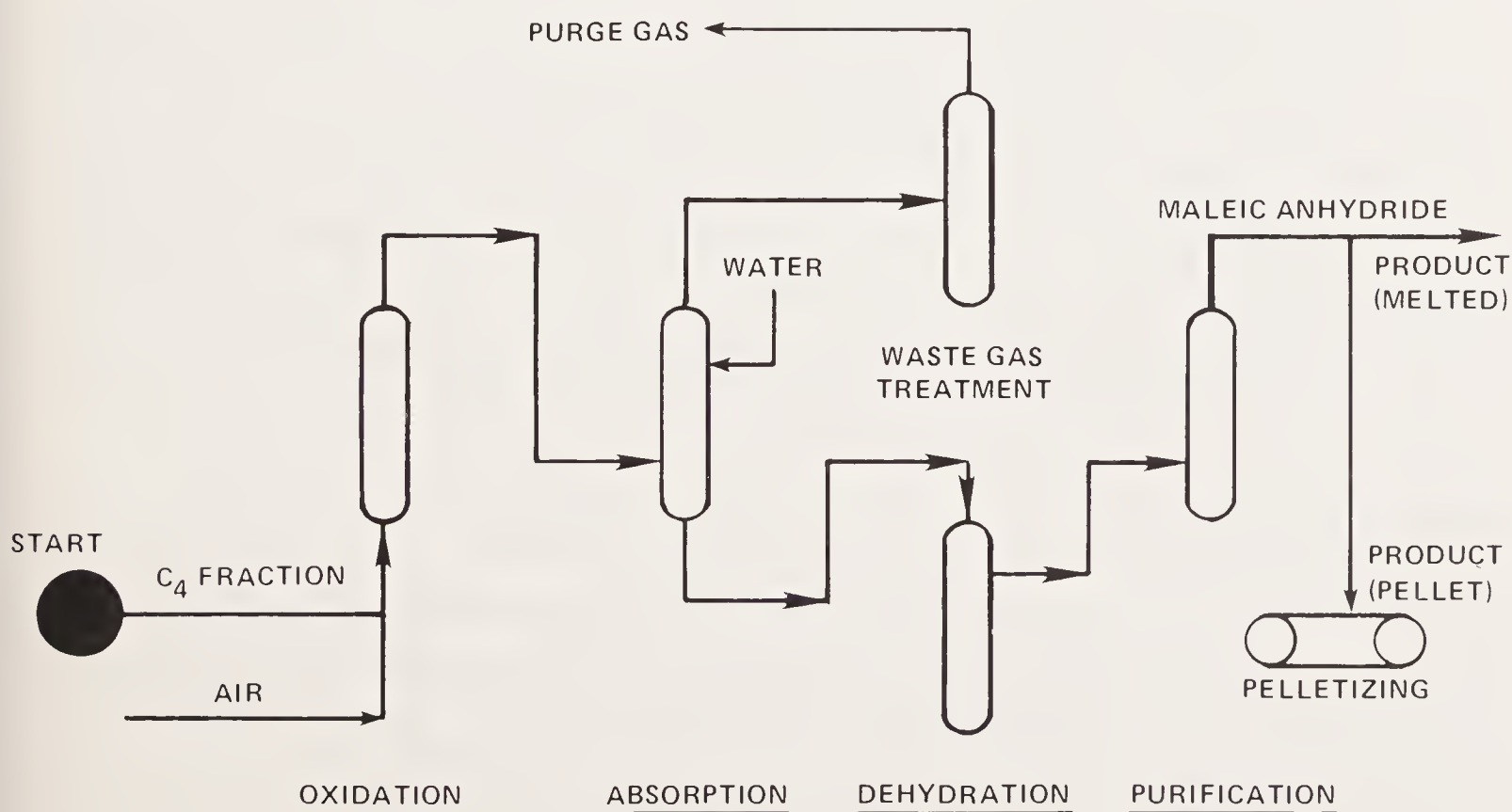


Fig. 2-5. Mitsubishi Chemical process. From Reference 67.

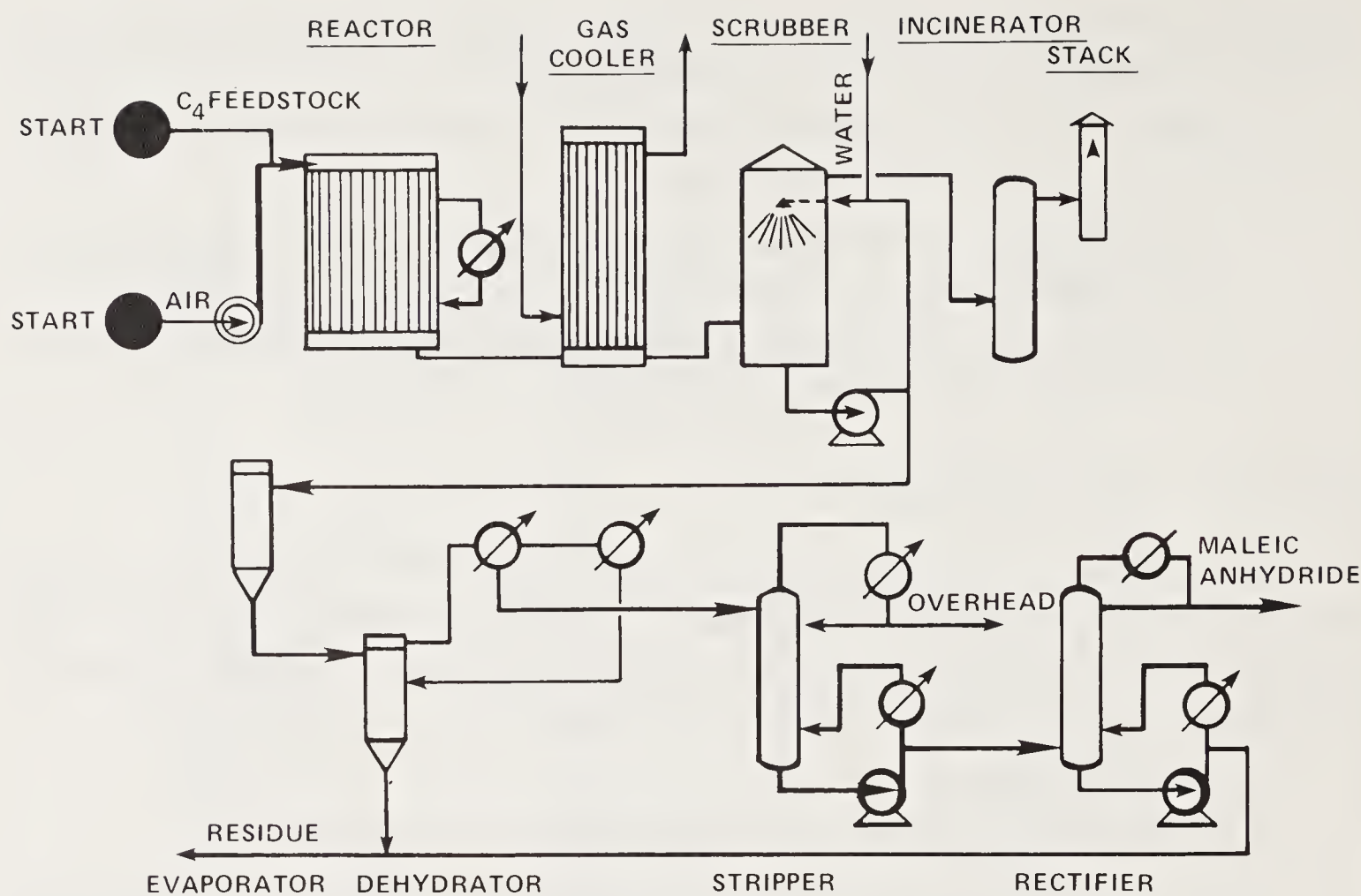


Fig. 2-6. BASF process. From Reference 69.

### 2.3.2.2. BASF Process

This process<sup>(61)</sup> (see Fig. 2-6) utilizes *n*-butenes and butadiene mixtures as raw material in a fixed bed tubular reactor, containing 10 000 tubes. The catalyst is vanadium based. The effluent gases from the reactor are cooled and then scrubbed with aqueous maleic acid solution. Film evaporators are used for the concentration of maleic acid solution and dehydration to MA. The latter is purified by continuous rectification. The yield of MA of 72 kg/100 kg of convertible hydrocarbons is claimed (42.6 mole %).

A waste gas incinerator eliminates pollution problems.

### 2.3.3. MA from Phthalic Anhydride Manufacture

During the manufacture of phthalic anhydride from naphthalene and *o*-xylene, small amounts of MA, citraconic anhydrides, and benzoic acid are coproduced.<sup>(1,70,71)</sup> MA comprises 6% of the product.<sup>(19)</sup> In some cases, after removal of phthalic anhydride by condensation, the exhaust gases are scrubbed with water. In many cases, the aqueous solution of maleic acid is recovered in the form of fumaric acid. Koppers in the United States recovers 10 MM lb of MA from the phthalic plant.<sup>(72)</sup>

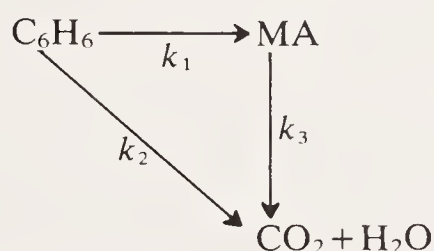


Since the boiling point of MA and citraconic anhydride are 199°C and 213°C, respectively, a small amount of citraconic anhydride always accompanies the distilled MA.<sup>(71)</sup> This lowers the melting point of MA slightly.

## 2.4. CHEMISTRY OF MA FROM BENZENE

Partial oxidation of benzene with air or oxygen in the gas phase produces MA, carbon monoxide, carbon dioxide, and water. Small amounts of other by-products such as phenol,<sup>(33)</sup> quinone,<sup>(29,30,73)</sup> diphenyl,<sup>(32)</sup> etc. have been claimed. The majority of studies have employed vanadium oxides or some combination thereof as a catalyst. The reaction is highly exothermic and can maintain itself with proper heat removal. An uncontrolled reaction may give poor selectivities and may even lead to combustion.

Although there are differences among various schools regarding the nature of reaction intermediates, a simplified generalized scheme appears agreed on without regard to the intermediates. Thus the scheme assumes equilibrium steady state amounts of intermediates.



The scheme above recognizes that the combustion route is different from that producing MA since MA can oxidize further. Kinetic data by a number of authors generally agree with this scheme. At sufficiently high concentration of benzene,  $k_1$  and  $k_2$  are pseudo first order in benzene. The dependence of  $k_3$  on MA concentration is less clear. Dixon and Longfield<sup>(75)</sup> claim it to be zero order in the MA concentration in the range 1.5–3.0 mol % of MA in air. On the other hand, Hammar<sup>(76)</sup> and Dmuchovsky *et al.*<sup>(77)</sup> show all rates to be nearly first order. The latter authors observed a very close correlation between observed and calculated mole ratios of products at 330°C on oxides of V, Mo, and Ni on carborundum as a catalyst (see Fig. 2-7).

Hammar's<sup>(76)</sup> work suggests some dependence of  $k_1$  on mass-transfer rates. However, other workers, such as Dixon,<sup>(75)</sup> Mars,<sup>(78)</sup> Holsen,<sup>(79)</sup> and Dmuchovsky *et al.*<sup>(77)</sup> show no significant dependence. Dixon and Longfield<sup>(75)</sup> propose that this difference may be due to the catalysts with very low surface areas used by Hammar.

There are a few common features in the data on benzene oxidation to MA by various workers:

- Rate of benzene disappearance is first order.
- Rate of MA disappearance is largely first order.
- Ratio  $k_1/(k_1 + k_3)$  is in fair agreement.

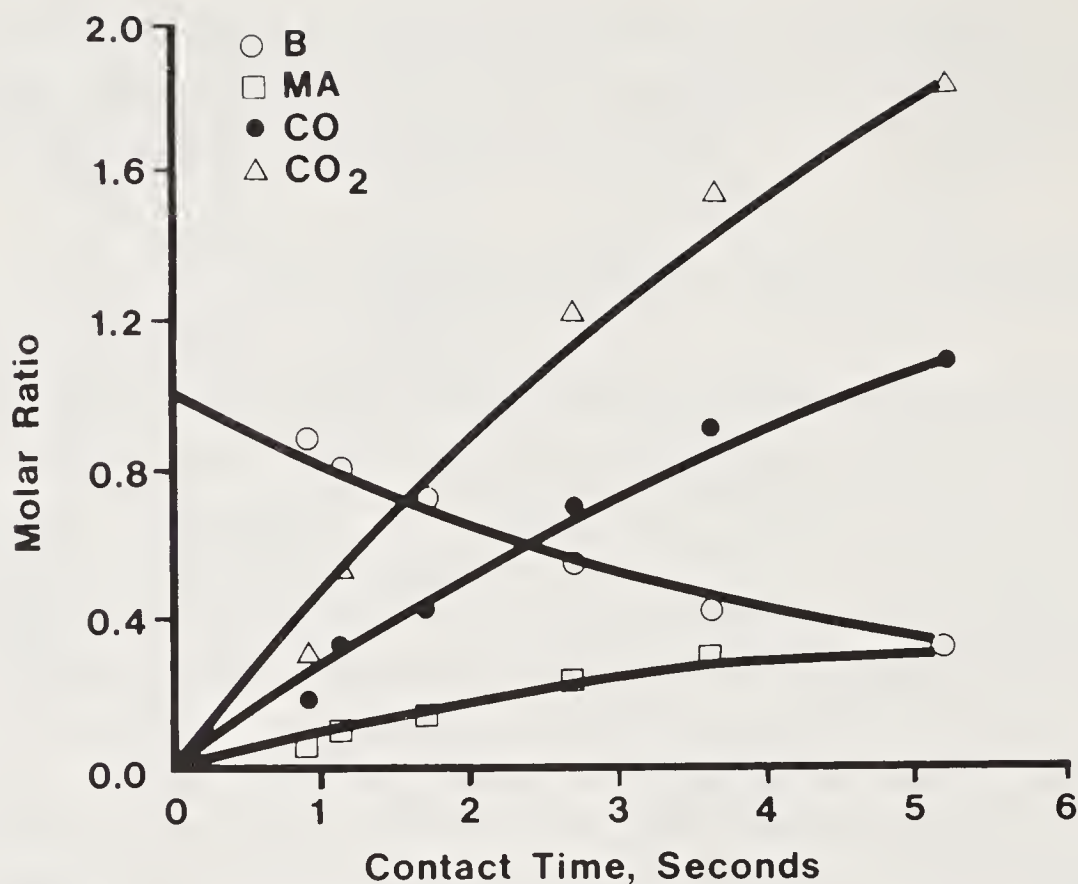


Fig. 2-7. Comparison of observed and calculated molar ratios of products to initial concentration of benzene as a function of time at 331°C. The points are experimental values. From Reference 77.

Dmuchovsky *et al.*<sup>(77)</sup> at Monsanto have studied the reaction in detail. As discussed earlier, their data are in agreement with the dual pathway mechanism. The activation parameters obtained are given in Table 2.1. It is argued that:

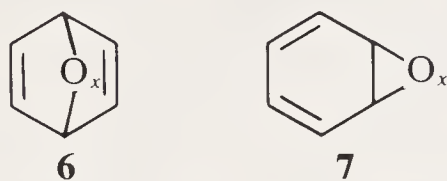
- Probably, the rate limiting step for both pathways is the same.
- The respective activated complexes should be different.
- Catalyst surface is saturated with oxygen atoms or molecules.
- The rate-limiting step may be the interaction of benzene with oxygen film on the catalyst surface.

The last two items are well corroborated in the work of Hayasky *et al.*<sup>(80)</sup> whose data on benzene order fit the Hinshelwood mechanism<sup>(80)</sup> for diffusion-limited reactions.

Table 2.1. Values of the Arrhenius Parameters

	$\log A$ ( $s^{-1}$ )	$E$ (kcal/mole)
$k_1$	11.7	$35 \pm 2$
$k_2$	0.4	$4.9 \pm 0.5$
$k_3$	8.4	$26 \pm 2$

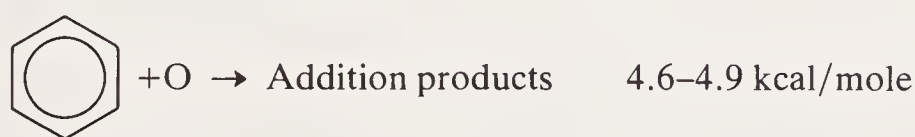
Based on these, Dmuchovsky *et al.*<sup>(77)</sup> propose that the two pathways followed are through the two activated complexes formed by 1, 2 and 1, 4 addition of some undefined oxygen species to benzene.



This suggests that structure **7** with 3–3.5 kcal resonance stabilization is lower in energy than **6**. Complex **6** is a precursor to MA whereas **7** leads to the combustion products. In Table 2.1, the MA-forming reaction demonstrated higher activation energy. The validity of this suggestion can be possibly verified through the study of kinetic isotope effects. In the hydroxylation or any such mechanism involving initial C-scission, the isotope effect would be much larger than that in 1,2–1,4 addition mechanism. In the Dmuchovsky *et al.*<sup>(77)</sup> mechanism, isotope effects would be only secondary and hence small.

The role of catalyst, although not understood clearly, is important since completely different products are formed in the gas-phase reaction of benzene with atomic oxygen.<sup>(81)</sup> This suggests further that free atomic oxygen is not important but absorbed oxygen atoms cannot be ruled out.

An interesting suggestion has been forwarded<sup>(77)</sup> toward explaining the oxygen species. It is known that activation energies for vanadium oxide-catalyzed oxidations of benzene, toluene, and naphthalene are all approximately 29 kcal/mole.<sup>(75)</sup> This energy is close to the sum of the energies for the following two processes:



However, there is no clear description of the nature of the oxygen species in the second step.<sup>(77)</sup> If one assumes atomic oxygen, the products, as mentioned, are known to be different.<sup>(81)</sup> Hayasky *et al.*<sup>(80)</sup> also showed different rates of  $\text{O}_2$  absorption in the oxidation of benzene, toluene, and naphthalene and suggested that different catalyst sites are involved. This questions the generalized mechanism for all aromatics.

## 2.5. CHEMISTRY OF MA FROM $\text{C}_4$ HYDROCARBONS

The alternate commercially practiced route to MA uses *n*-butane, butene-1, butene-2, and butadiene or a mixture thereof. The mechanism of the overall process is less well understood. The process is also complicated by the number



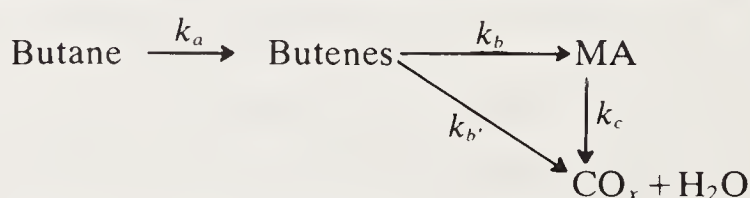
of by-products formed such as crotonaldehyde, furan, and crotonic acid. Starting from butane, by-product butenes and butadiene are also observed. In addition, acetic acid, methylvinyl ketone, acetaldehyde, formaldehyde, CO, CO<sub>2</sub>, glyoxalic acid, etc., have been reported in the literature. The stoichiometry for MA production are as follows:



Bisset and Benson,<sup>(82)</sup> at DuPont, studied the partial oxidation of *n*-butane using a cobalt molybdate catalyst. The MA formation kinetics suggested that there were two consecutive first-order reactions:

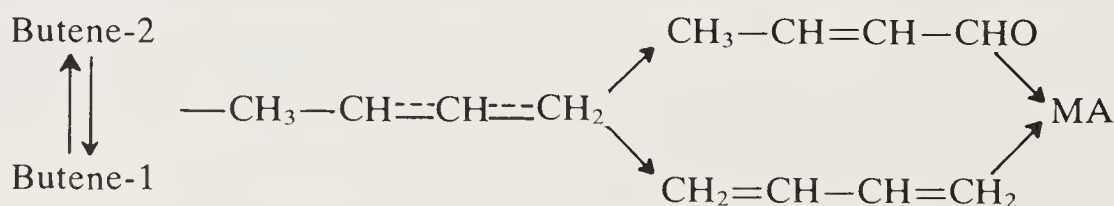
- dehydrogenation of *n*-butane to butenes
- decomposition of MA

The intermediate oxidations are so rapid that they have no significant influence on the overall kinetics. Ai and coworkers<sup>(83)</sup> also show that overall oxidation is much faster than isomerization as shown in Fig. 2-8.



Dehydrogenation of butane to a mixture of butenes given by the rate constant  $k_a$  is first order in butane and independent of the oxygen concentration. Since higher yields of MA are obtained from *cis*-butene-2 than the mixture of *cis* and *trans* isomers, the stereochemistry of the butene formation may be important in determining  $k_b$  vs  $k_{b'}$ .<sup>(84)</sup>

Sampson and Shooter,<sup>(85)</sup> from their study on vanadium oxide/phosphorus pentoxide catalyzed oxidation of *n*-butane, suggest that there are two potential routes of MA; one via crotonaldehyde and the other via butadiene. Furan has also been suggested as an intermediate in the sequence.<sup>(24)</sup>



Akimoto and Echigoya,<sup>(86,87)</sup> based on their study of MoO<sub>3</sub> + TiO<sub>2</sub> catalyzed oxidation of butadiene, dihydrofuran (2, 5-DHF), and furan, argue that butadiene oxidizes to MA via two pathways:

- via dihydrofuran and furan
- via dihydrofuran without the furan intermediate



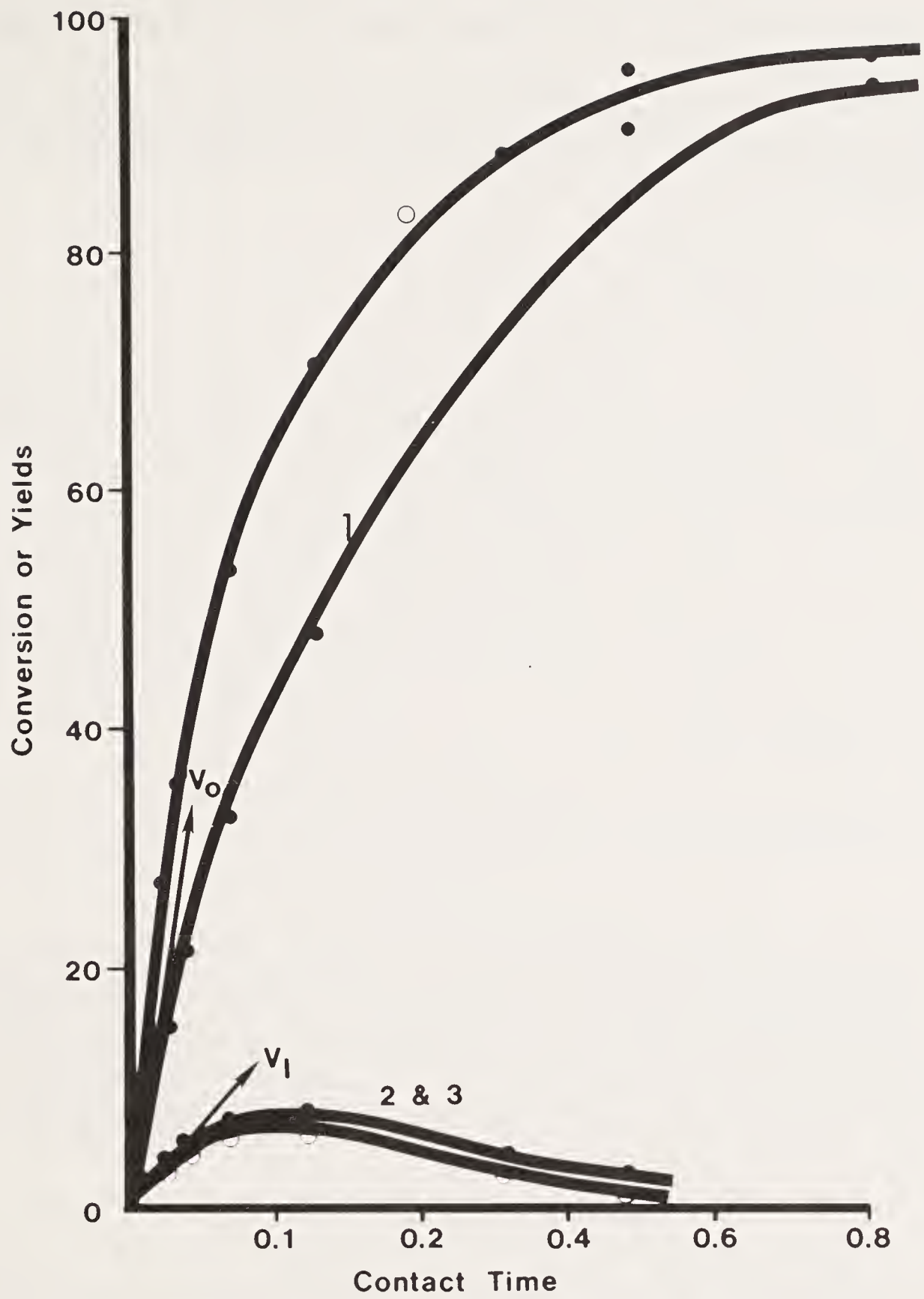
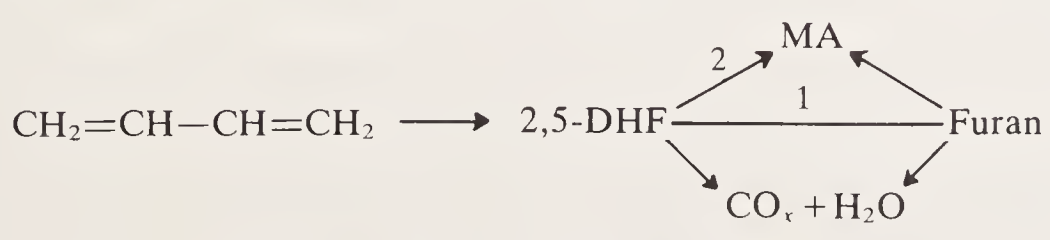


Fig. 2-8. Oxidation and isomerization of *cis*-Butene-2<sup>(83)</sup>: (0) = Conversion of *cis*-Butene-2; (1) = Sum of oxidation products w.r.t. butenes; (2) & (3) = Yields of *trans*-butene-2 and butene-1.

Their scheme is shown below:



The formation of 2,5-dihydrofuran is the rate-determining step. They<sup>(86,87)</sup>

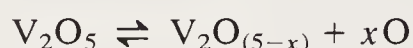
further suggest that lower temperatures favor route 1 whereas higher temperatures favor route 2.

Understanding of the mechanism of C<sub>4</sub> oxidation to MA is far from complete. The interested reader is referred to the original articles on this and related systems.<sup>(101-106,108)</sup>

## 2.6. CATALYSTS AND THEIR ROLE

In the almost 60 years since the first patent on MA production by Weiss and Downs,<sup>(88)</sup> a flood of patent and nonpatent literature has been published. In the benzene oxidation route, vanadium oxide stands out to be the most common feature of all the catalysts. It appears that in the commercial production of MA from benzene, vanadium oxide or cocatalyst promoted vanadium oxide over a support is used (except SAVA<sup>(65)</sup> process). Typical promoters used are oxides or salts of the following elements: Mo, W, Bi, Sn, P, Ag, Cu, Na, B, Ti, and Ni. The V + Mo is most common. Other elements may also act as modifiers (see Ref. 15).

There has been some effort to understand how vanadium contributes to the oxidation. It is generally assumed that V<sub>2</sub>O<sub>5</sub> goes through the following reversible process during the reaction.



Reduction of the V<sup>5+</sup> at the surface is brought about by the hydrocarbon. Electron paramagnetic resonance (EPR) studies on V<sub>2</sub>O<sub>5</sub> catalysts show the presence of unpaired electrons.<sup>(89)</sup> The observed paramagnetic species are believed to be associated with the metal and not with O<sub>2</sub>. It has been postulated that benzene is absorbed on the surface, followed by abstraction of a hydrogen atom to form a surface radical.

The role of MoO<sub>3</sub> as a promoter has been explained as a moderator for benzene oxidation. Bhattacharya and Venkataraman<sup>(29)</sup> studied a variety of vanadium oxide-based catalysts. They concluded that, under their conditions, the best yields of MA were obtained using the composition V<sub>2</sub>O<sub>5</sub> (1-2.3):MoO<sub>3</sub> (1.0), supported on kieselguhr, with 5% cobalt oxide as a promoter.

It has been shown by Bielanski and Inglet<sup>(90,91)</sup> that the concentration of V<sup>4+</sup> species produced is affected by the concentration of MoO<sub>3</sub> in the catalyst (see Fig. 2-9). Furthermore, the rate of V<sup>5+</sup> to V<sup>4+</sup> conversion is also dependent on the amount of Mo in the composition. The rate of benzene oxidation versus V<sup>4+</sup> concentration is given in Fig. 2-10. A parallel is quite evident, suggesting that the rate of MA production is a function of V<sup>4+</sup> concentration, such that in the equation above,  $x = 1$ . In Fig. 2-11, selectivity to MA at half benzene conversion is given as a function of V<sup>4+</sup> concentration.

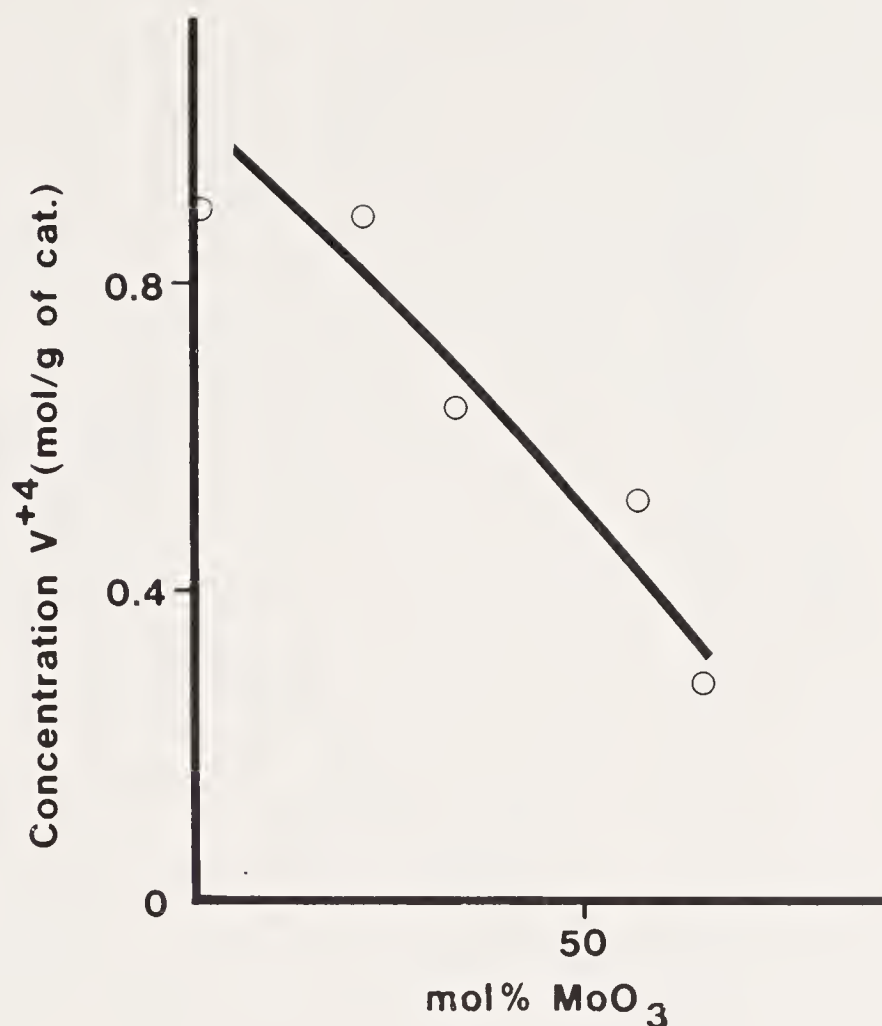
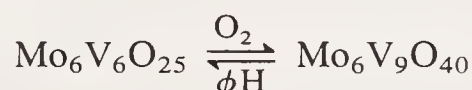


Fig. 2-9. The concentration of tetravalent vanadium reached after prolonged activation versus composition of the catalysts. From Reference 91.

From these results, it appears that MoO<sub>3</sub> is a moderator and acts by controlling the concentration of the active species.

Ioffe and coworkers<sup>(92)</sup> used x-ray studies to follow the vanadia-molybdena catalyst utilized for benzene oxidation. They claim that the activity of the catalyst parallels formation of a solid solution of MoO<sub>3</sub> in the V<sub>2</sub>O<sub>5</sub> lattice. They determined a maximum around 25–30 mole % MoO<sub>3</sub>. Munch and Pierron<sup>(93)</sup> at Monsanto claim that at higher temperatures MoO<sub>3</sub>–V<sub>2</sub>O<sub>5</sub> can form compound oxides and propose the following equilibrium and dispute the claims of solid solutions.



All the commercial catalysts studied had these compounds in them. Since the pure materials were less active, no claims on activity could be made. Butler and Weston<sup>(74)</sup> argue that the real catalytically active agent is V<sub>2</sub>O<sub>4.34</sub> or V<sub>6</sub>O<sub>13</sub>. This oxide, formed at the surface, will be in equilibrium with V<sub>2</sub>O<sub>4</sub> and V<sub>2</sub>O<sub>5</sub>. Further discussions on this aspect are beyond the scope of this work. The interested reader is recommended the excellent articles by the original authors.

The work on catalysts for C<sub>4</sub> hydrocarbons has been relatively recent. Ai and Ikawa<sup>(94)</sup> have correlated acid-base properties of the catalyst with activities in a Mo–P–Bi catalyst with varying bismuth content. They suggest that increasing Bi content decreases the acidity. The formation of acid (anhydride) is favored over a low-Bi-containing catalyst, i.e., high-acidity catalyst.



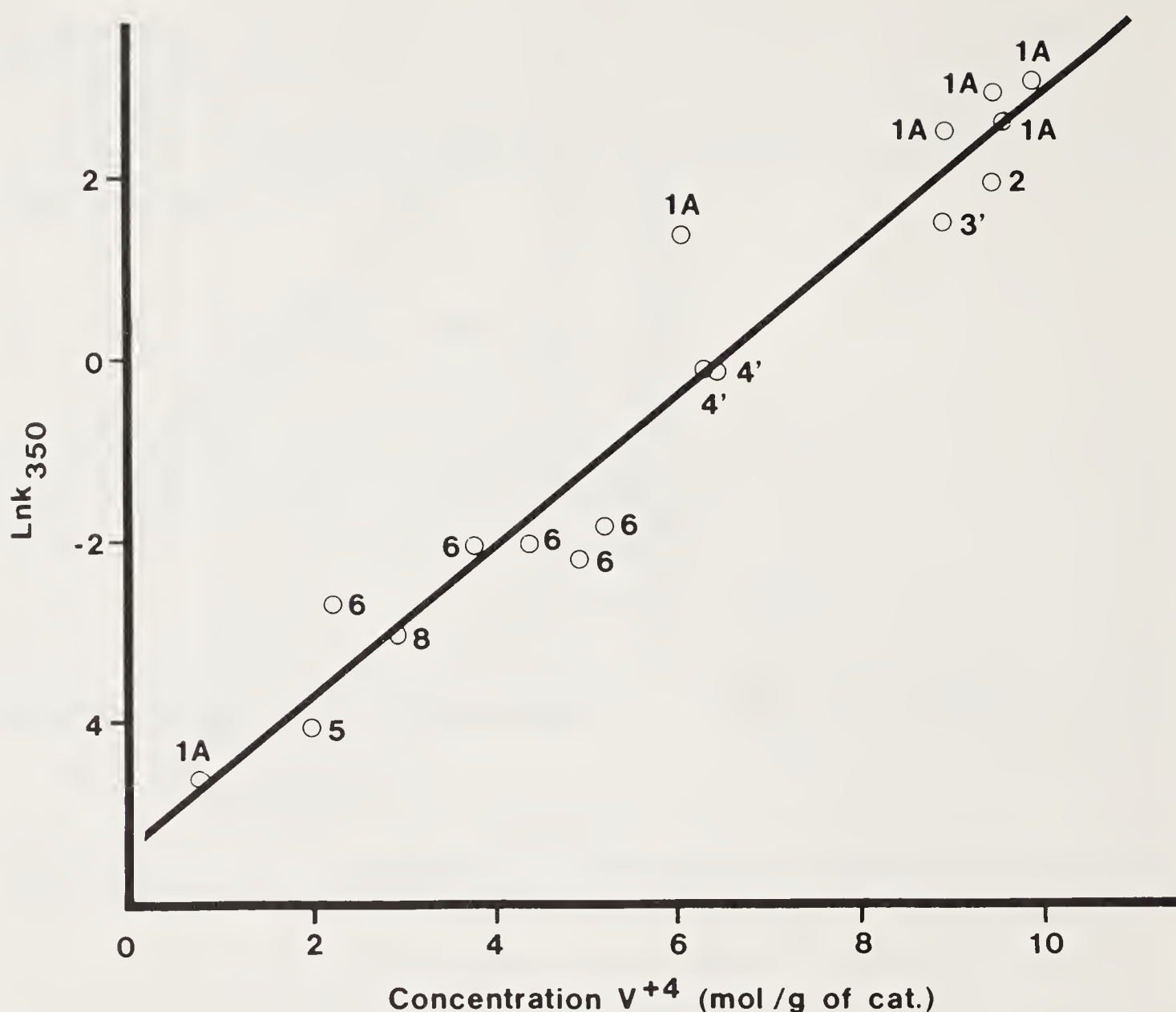


Fig. 2-10. Velocity constant  $k_{350}$  of the reaction of benzene oxidation corresponding to a temperature of 350°C as the function of  $V^{4+}$  concentration in the catalyst. From Reference 90.

The high-Bi systems are favorable for dehydrogenation activity. Similarly in a Ti-V-P system,<sup>(95)</sup> Ai showed that  $P_2O_5$  content increases the acidity of the catalyst which favors MA formation from butadiene up to a point, but impedes the dehydrogenation selectivity of butene-1 to the diene (see Fig. 2-12).

Emig *et al.*,<sup>(114)</sup> on the other hand, have studied butene oxidation using V + P oxide catalysts. They suggest no effect of V/P ratio on the yield of MA. The main factors affecting the latter were time and temperature of calcination.

Akimoto and Echigoya<sup>(86,87)</sup> have studied the oxidation of butadiene on a Mo-Ti catalyst. They observed a linear relationship between the concentration of  $Mo^{5+}$  species and rate of  $CO_2$  formation. However, rate of MA formation increases nonlinearly. It was concluded that only one  $Mo^{5+}$  site is involved in the rate-controlling step during  $CO_2$  formation, whereas more than one site was necessary for MA formation. They also conclude from their

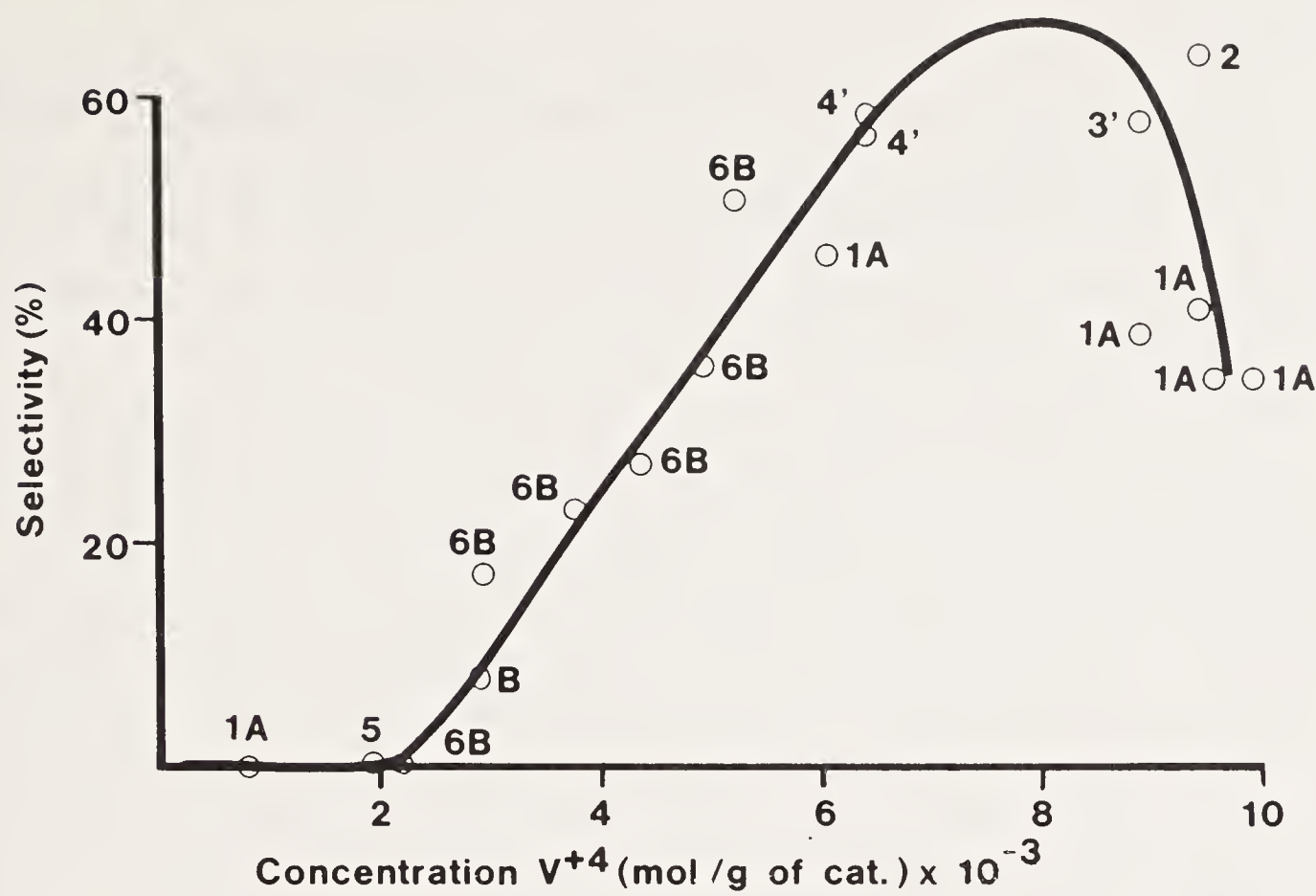


Fig. 2-11. Selectivity  $S$  (%) versus concentration of  $V^{4+}$  in the catalysts. From Reference 90.

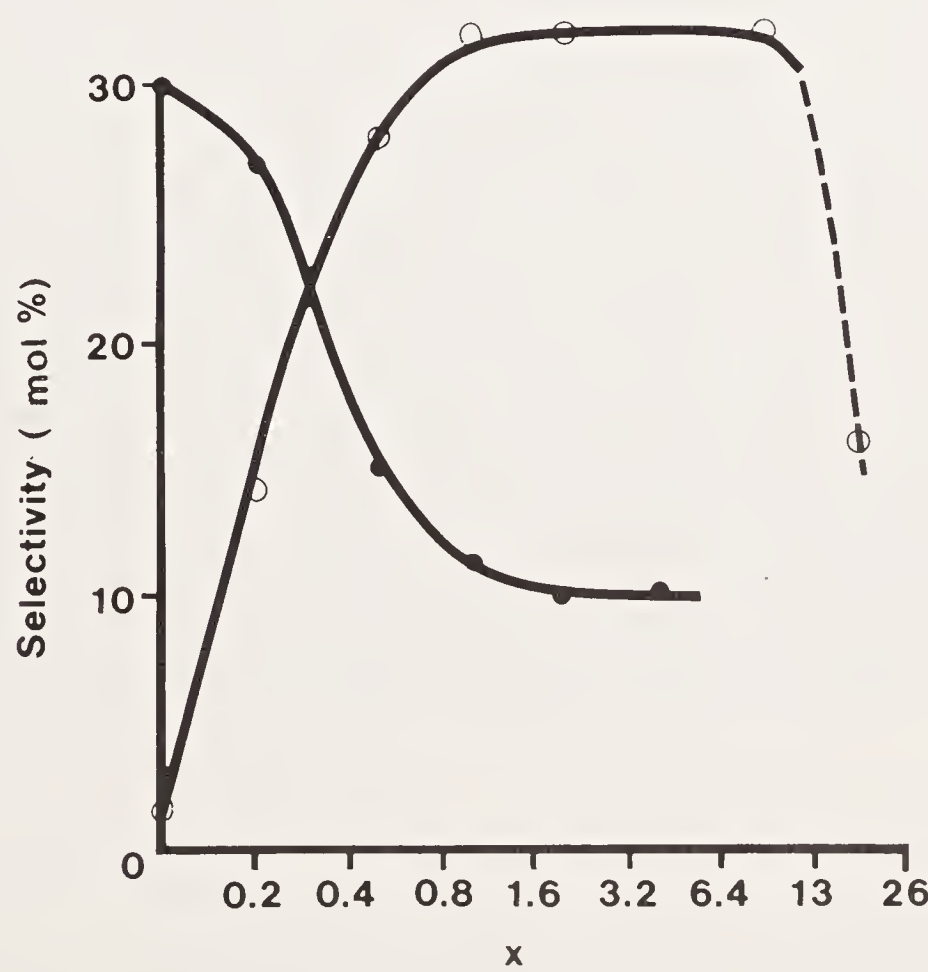


Fig. 2-12. Selectivity as a function of the  $P_2O_5$  content ( $x$ ): (○) Selectivity of butadiene to MA; (●) selectivity of butene-1 to butadiene. From Reference 95.

data that:

- Oxygen species on Mo ions and butadiene absorbed on  $\text{Ti}^{4+}$  to form carbon dioxide.
- Butadiene species absorbed on  $\text{Mo}^{5+}$  site yield MA.

Again due to the scope of this work, we recommend the original references by Akimoto and Echigoya<sup>(96,97,98,106)</sup> to the interested reader.

Small amounts of metallic salts such as Ni, Ti,  $\text{P}_2\text{O}_5$ , K, Co, and Li, have been used as modifiers. There is no clear understanding of their function except that they somehow modify the oxidation of the hydrocarbon, intermediates, or the product, thereby improving the selectivity to the product.<sup>(19)</sup>

For benzene oxidation, V + Mo oxides are usually catalysts. Inert supports such as silica, alumina, alundum, quartz, pumice, metallicaluminum, etc. have been tried. High-surface-area supports are observed to have a deleterious effect on the benzene oxidation to MA. A low-porosity-catalyst support may peel off, particularly so in a fluidized bed. Catalyst supports of medium porosity are employed.<sup>(15,19)</sup>

For  $\text{C}_4$  processes, V + P oxides with modifiers appears common, based on the patent literature. Recently, a nonvanadium-containing catalyst has been claimed to give near quantitative conversion of butadiene and to give a 75% yield of MA.<sup>(113)</sup>

## 2.7. EPILOGUE

It may be of interest to observe that the optimum conditions for a catalyst may not be the ones utilized in a commercial production. This is because several other important variables enter into consideration in addition to the optimum yield since the main determinant is the economics of the overall process. Toward this end, the state of technological development plays a very important role because product recovery, energy needs of the process, efficient heat removal, catalyst life, etc. enter as variables in addition to raw material and labor costs. The direct recovery of MA from the exhaust gases has played an important role in this connection. To make the collection technology commercially and economically viable, a certain minimum concentration of MA in the exhaust gases is required. Allowance for this and other technological factors may dictate that a process not be run at its optimum yield level.



# 3

## REACTIONS OF FUNCTIONAL GROUPS

### 3.1. INTRODUCTION

The unsaturated linkage in maleic anhydride is activated due to conjugation with the carboxyl grouping. As a result, not only does maleic anhydride undergo reactions that are typical of an olefin, but, in addition, it enters into reactions such as nucleophilic addition. The electrophilic character of the double bond produced by conjugation plays a significant role in a number of reactions of MA including Diels–Alder, some photoreactions, and so on. Thus, in addition to its internal anhydride function, MA possesses an activity at the very reactive double bond and this property separates it from other anhydrides such as phthalic, succinic, etc. The complete importance of the olefin linkage is hard to ascertain in both monomeric and polymeric products derived from MA. It is sufficient to say that this unsaturation has played a major role in the products of various industries particularly in paints, varnishes, surfactants, lubricants, and agricultural products, just to name a few.

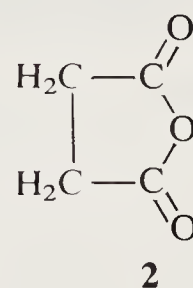
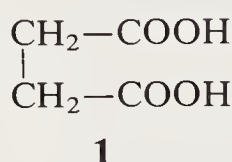
Since the unsaturation in MA is present in some MA derivatives, attention will be directed to the reaction of either MA or its simple derivatives, such as maleic acid, esters, or amides. These derivatives, as can be seen in this chapter, are relatively easy to obtain. A fact to remember is that often the reactivity of its derivative is less than MA. However, this is hardly a detriment, since many times a number of other factors such as ease of handling, convenience, and available routes to the desired end take precedence. In this connection, reactions at the anhydride function are useful since ester, amic acids, and imides are made by the participation of the anhydride function. This possibility of independent manipulation lends MA versatility and uniqueness. Therefore, in this chapter, in addition to the reactions of MA, reactions of common derivatives of MA are used where synthetically or mechanistically pertinent.

### 3.2. REACTIONS OF OLEFINIC FUNCTIONS

#### 3.2.1. Hydrogenation to Succinic Acid

Catalytic hydrogenation of the olefinic bond in MA yields succinic anhydride. The same reaction can be achieved on any MA derivative. Succinic

acid **1** and anhydride (SA) **2** are commercially made this way.<sup>(1)</sup> A number of hydrogenation catalysts can be successfully employed for this purpose.<sup>(2,3,18,19)</sup>

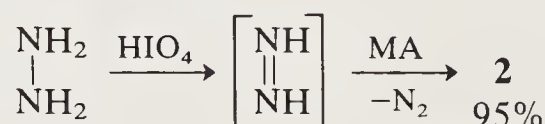


Allen *et al.*<sup>(2)</sup> have shown that the disodium salt of maleic acid can be reduced with Raney nickel at 100°C and 2 500 psi. The yield of succinic acid after acidification is near quantitative. Among other catalysts, platinum metals could be equally effective in bringing about the hydrogenation under milder conditions<sup>(3)</sup> since **2** is a by-product in the reduction of MA to  $\gamma$ -butyrolactone and THF.<sup>(13)</sup> (See Chapter 7.)

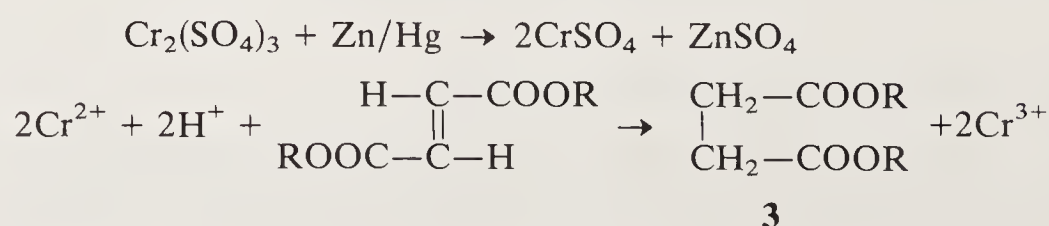
Electrolytic reduction of maleic derivatives can also be used to produce the corresponding succinic derivatives. Takahashi and Elving<sup>(4)</sup> have reported polarographic reductions of MA, maleate, and fumarate esters, and Elving and Teitelbaum<sup>(5)</sup> have described the effect of pH on the polarographic reduction in protic solvents. Ruiz and Avila<sup>(289)</sup> have also examined these pH effects on maleic and fumaric acids recently.

In their study of maleic acid and fumaric acid, Takahashi and Elving<sup>(4)</sup> reported that the two showed identical behavior in pyridine solution. Since extremely dilute solutions are employed, it may be expected that actually maleic acid completely isomerized to fumaric acid before the measurement, since pyridine is a known catalyst for the process.<sup>(39)</sup> Isolation or spectral studies, therefore, may be revealing.

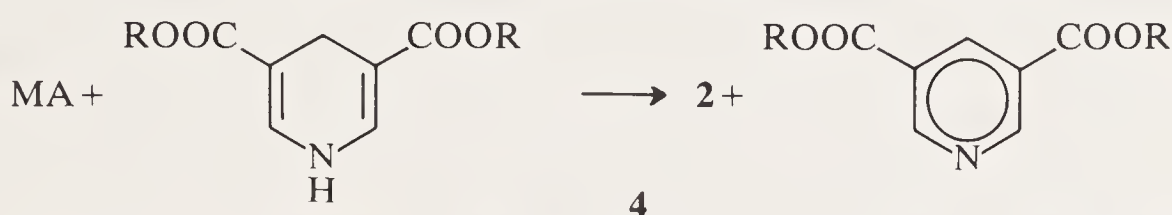
Hoffman and Schessing<sup>(6)</sup> have reported the use of diimide as a reducing agent. The latter was prepared by periodate oxidation of hydrazine *in situ*.<sup>(7)</sup>



Chromous salt has also been used for reducing unsaturation in diethyl fumarate. The chromous salt is made by reducing chromium (3+) salt with zinc amalgam. A yield of 88–94% has been reported for diethyl succinate **3**.<sup>(8)</sup> Mild reduction using zinc/sulfuric acid has also been reported.<sup>(9)</sup>

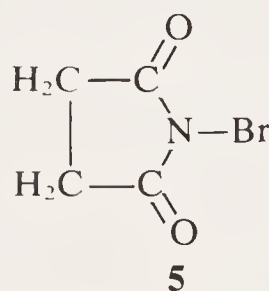


Hydrogenation of the olefinic system in MA and esters can also be achieved by transfer hydrogenation. Braude *et al.*<sup>(10)</sup> and Bandi *et al.*<sup>(11)</sup> have studied the Hantzsch ester **4** as a hydrogen donor. Nearly all the hydrogen was transferred to the substrate. The results in Table 3.1 were obtained by Braude *et al.*<sup>(10)</sup> when using equimolar quantities of MA and Hantzsch ester.



The use of 1,2-dihydroquinoline as a source of hydrogen gave amide formation. Braude *et al.*<sup>(10)</sup> also note that dimethyl maleate and dimethyl fumarate yield succinate ester when heated with Hantzsch ester **4**. However, both react more slowly than MA and a higher reaction temperature is required.

Succinic acid *per se* does not represent a large volume consumer of MA. However, it finds a variety of uses in chemical applications. Its most important derivative widely known to synthetic organic chemists is *N*-bromosuccinimide **5**. The latter is used as a selective brominating agent.<sup>(12)</sup> The active halogen atom can also be supplied using *N*-chlorosuccinimide for purification of drinking water.



One reaction of dialkyl succinate—namely, Stobbe condensation—has played a key role in the synthesis of important pharmaceuticals. The reaction involves a base-catalyzed condensation of aldehydes or ketones with succinate esters **3** to yield itaconic acid derivatives **6**.<sup>(16,17)</sup> Numerous pharmaceutical

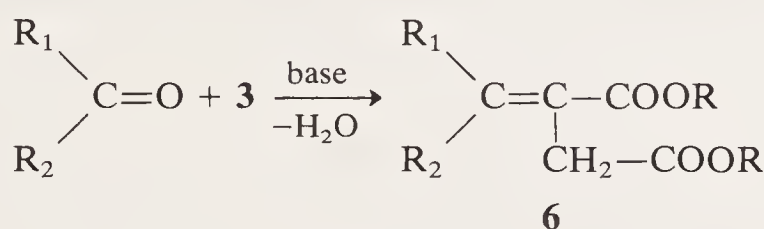


Table 3.1. Reduction of MA with Hantzsch Ester<sup>a</sup>

Temperature	Time	SA (Selectivity)	% Reagent oxidized
99°C	70 h	93	95%
66°C	70 min	77	80%
101°C	30 min	91	95%

<sup>a</sup> From Reference 10.

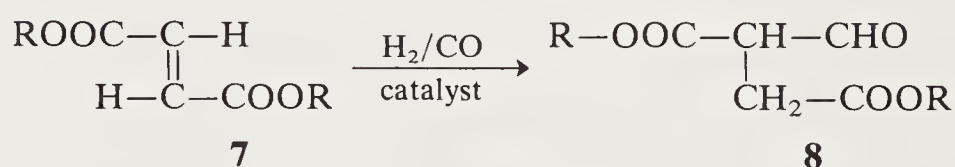


and other applications are known for this reaction. The reaction is quite unique to succinate esters<sup>(16,17)</sup> since a lactone ring is probably formed as an intermediate.

The dialkyl succinates are good plasticizers for vinyl chloride polymers and copolymers and for cellulose derivatives. SA is also used in the manufacture of alkyd resin to impart flexibility, elasticity, and water resistance.<sup>(14)</sup> In addition, it finds numerous applications in the field of adhesives, elastomers, lubricants, pharmaceuticals, pesticides, and epoxy and other resins. Succinic acid is also used as a food acidulant and has been placed on the GRAS (generally regarded as safe) list by the FDA.<sup>(15)</sup>

### 3.2.2. Hydroformylation

The esters of maleic acid can be hydroformylated to obtain the formyl derivative **8**. Adkins and Kresk<sup>(20)</sup> reported the reaction of diethyl fumerate **7**. In the presence of a cobalt catalyst at 150°C and a total pressure of 4 800 psi of carbon monoxide and hydrogen (2:1) CO:H<sub>2</sub>, the Oxo product, diethyl formylsuccinate **8** (R = Et), was formed in a 51% yield. The fate of the remaining material was not specified but it is believed to have mostly converted to diethyl succinate by hydrogenation (see below).



Umemura and Ikeda<sup>(21)</sup> have described much better yields of the formyl derivative **8** in a Japanese patent. In their case, lower temperatures 70–120°C and lower total pressure [150 atm at room temperature (RT)] of CO:H<sub>2</sub> having a 1:1 ratio was employed. Thus dimethyl maleate at 100°C and 115-atm pressure gave an 83% yield of the formyl product **8** (R = Me). Dimethyl succinate was formed as a by-product. Their data are summarized in Table 3.2. Evidently temperatures >110°C are deleterious to the selectivity of the formyl derivative **8** and hydrogenation to succinate increases. Direct hydroformylation potentially with rhodium catalysts under mild conditions may significantly reduce hydrogenation.

The potential of these products is almost unexplored. Direct hydroformylation of MA has not been investigated, and the hydrogenation of the formyl derivative **8** to the alcohol has the making of a polyester or a lactone.

### 3.2.3. Addition of Water

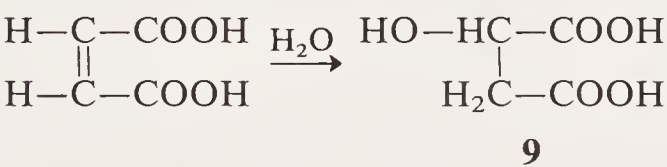
Maleic anhydride or its derivatives undergo the usual reactions of an olefin. Maleic acid, for instance, can be hydrated to yield malic acid **9**.<sup>(22)</sup> This

Table 3.2. Hydroformylation of Esters of MA<sup>a</sup>

					% Selectivity	
Raw material Ester <sup>b</sup>	partial pressure of gases <sup>c</sup>		Temperature	Conversion	8	DMS
	CO	H <sub>2</sub>			R = Me	R = Me
DMM	53	46	80	90	81	6.5
DMM	52	43	120	100	70	25
DMF	56	48	100	100	72	15
DMM	35	50	95	100	79	10
DMM	40	40	110	100	82	5
DMM	60	60	150	100	45	40
DMM	73	73	145	100	51	41

<sup>a</sup> From Reference 21.  
<sup>b</sup> DMM = dimethyl maleate, DMF = dimethyl fumarate, DMS = dimethyl succinate.  
<sup>c</sup> At room temperature.

hydration is relatively easier for maleic acid than other olefins due to the double-bond activation by conjugation with the acid functions. As is apparent in structure **9**, an asymmetric center is created during hydration. Commonly, a racemic mixture is produced, as would be expected in conditions not specifically designed for asymmetric synthesis. The hydration is usually carried out at 180°C in a corrosion-resistant pressure vessel.



The naturally occurring form is *l*-malic acid. The latter occurs in a number of fruits including apple, apricot, banana, cherry, and grape. It may be remembered that MA was first isolated from the decomposition of malic acid.

When *l*-malic acid is desired, hydration may be carried out using micro-organisms. Degen *et al.*<sup>(23)</sup> have recently claimed a 75% yield of *l*-malic acid when hydration of fumaric acid was assisted by paracobactrum Nos. 743, 745, and 746.

To obtain *l*-malic acid from a usual synthesis giving a mixture of *d* and *l* stereoisomers, a resolution is necessary. This is generally achieved by crystallization of the cinchonine salt of malic acid. By this method, cinchonine, which is an optically active amine, forms a mixture of diastereomeric salts with different solubility characteristics. Other optically active amines may also be utilized.

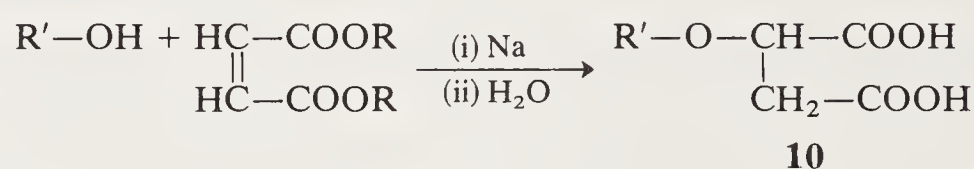
The natural occurrence of malic acid gives it an easy acceptability as a food additive. It has been included on the GRAS list by the U.S. Food and Drug Administration.<sup>(24)</sup> Common applications of malic acid to this end are



as a flavoring agent and food acidulant. Among other uses, it is employed also as a specialty material for the preparation of certain phenolics, alkyds, and shellacs, to name a few. Furthermore, it has been used in pharmaceutical formulations.<sup>(25)</sup>

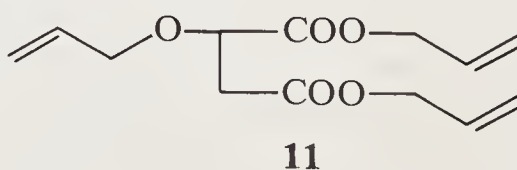
### 3.2.4. Addition of Alcohols

As would be obvious, the primary reaction of MA with alcohols is esterification. However, under the influence of a strong base such as sodium alcoholate, derivatives of MA, for example esters of MA, can add the elements of alcohol across the double bond. The production of alkoxysuccinic acids **10** was investigated by Purdie.<sup>(26,27)</sup>

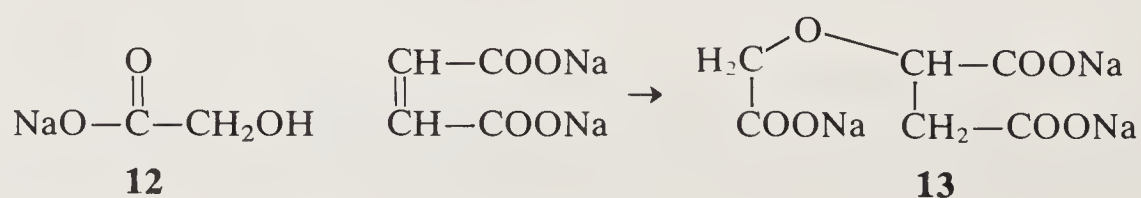


Ethanol reportedly gave a 60% yield of the adduct **10** ( $\text{R}' = \text{Et}$ ). Methanol and isobutyl alcohol were also reported to react. The reaction product of MA with methanol (probably the monomethyl maleate) on treatment with 2 equivalents of sodium in excess of methanol also gave 19% of the acid **10** ( $\text{R}' = \text{Me}$ ) isolated as its salt.

Dialkyl maleate reacts with an excess of allyl alcohol to yield a rather interesting monomer **11**.<sup>(28)</sup> Similarly, Kyrides<sup>(29)</sup> has reported the addition of sodium salts of *n*-decyl and *n*-dodecyl alcohols on diethyl maleate. Ester exchange may complicate the yields of these reactions due to the strongly basic character of sodium alkoxides. Weak bases such as fluoride ions may provide the selectivities. The fluoride ion is known to promote the Michael reaction without affecting transesterification of the carboxylic esters.<sup>(295)</sup>

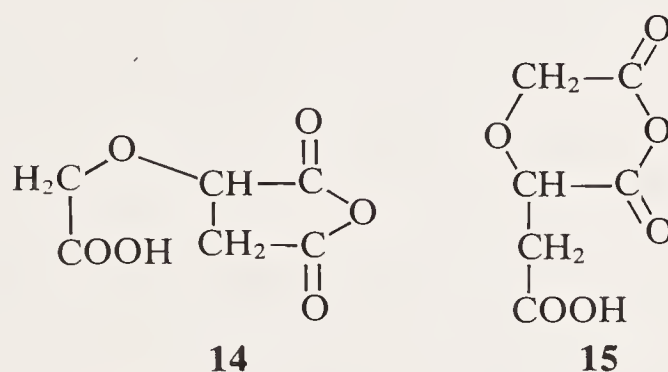


As was seen with Purdie's work, the diesters are not the only synthetically useful derivatives of MA for this purpose. Advantage is taken of the reaction of the sodium salts in the preparation of tri-sodium carboxymethyloxysuccinate **13**. The latter is prepared by the reaction of disodium maleate and sodium glycolate **12**.<sup>(30)</sup>



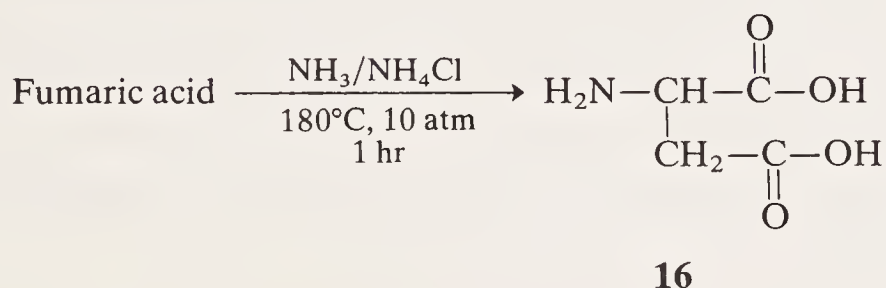


The products of this reaction have found uses as synthetic detergents and monomers. Carboxy methyloxysuccinic acid **13** has sequestering properties for  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions.<sup>(4,5,29-31,261)</sup> During the late 1960s and early 1970s, phosphate used as a builder for the detergents was alleged to contribute to eutrophication.<sup>(31)</sup> Among the new organic replacements for phosphate, **13** played an important role.<sup>(262)</sup> The anhydrides **14** and **15** obtained on dehydration have been proposed for application in food flavorings, detergent builders, surfactants, coatings, gasoline additives, etc.<sup>(31,32)</sup> The adducts made from decyl alcohol and dodecyl alcohol are also suggested as detergents, emulsifying agents for paints, latex, and flotation agents.

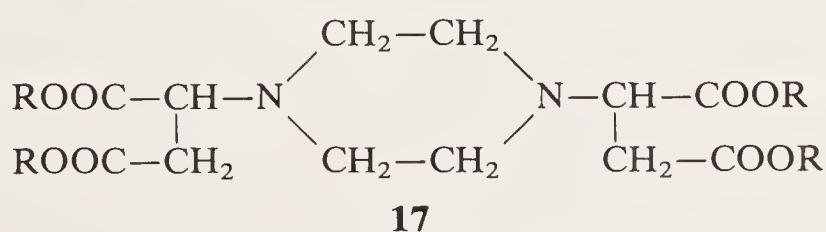


### 3.2.5. Addition of Amines

Maleic acid and its derivatives smoothly add ammonia and amines to yield aspartic acid derivatives. Fumaric acid, for example, yields aspartic acid **16** in a 60–65% yield when it is heated with an excess of ammonia in the presence of ammonium chloride.<sup>(33)</sup>

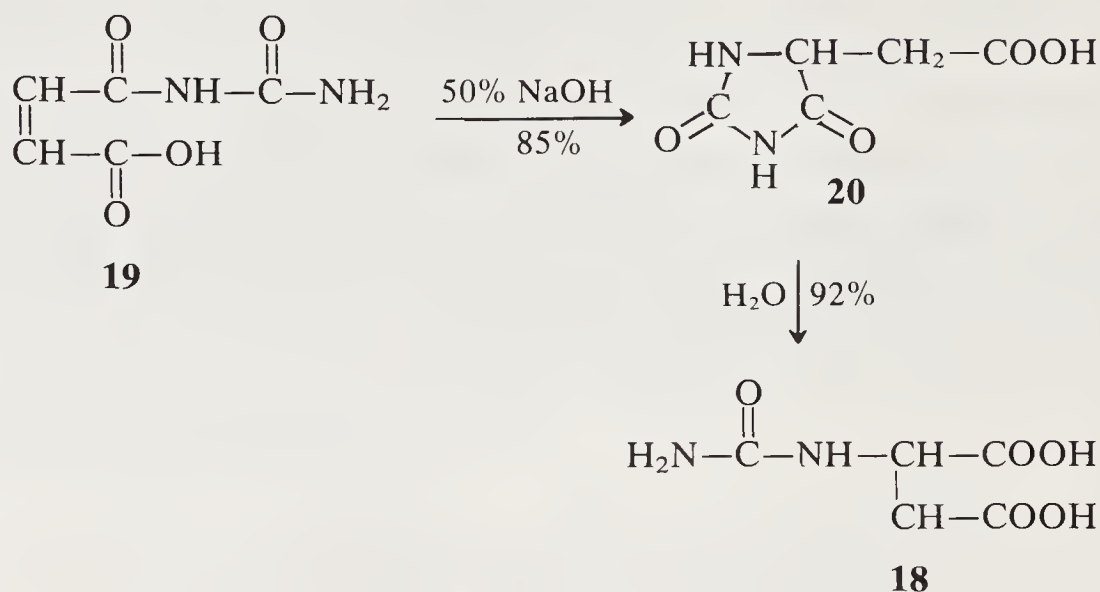


Substituted derivatives are prepared similarly,<sup>(34)</sup> the yields being generally modest.<sup>(35,36)</sup> Diamines similarly yield the bis-aspartyl derivative such as **17** on reaction with esters.<sup>(37)</sup>

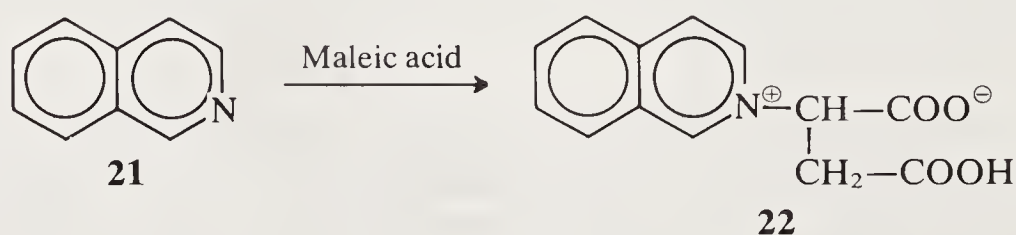


Hydrazine derivatives also react to give the bis addition products.<sup>(38)</sup>

An interesting aspartic acid derivative, namely, ureidosuccinic acid **18**, has been made recently as shown in the following scheme.<sup>(40)</sup> Compound **19** can be prepared by the reaction of urea with MA (see section 3.4.4.1).



Isoquinoline **21**, on heating with maleic acid, reacts to give a betaine **22**.<sup>(41)</sup> However, these and similar reactions have far reaching ramifications and are dealt with elsewhere. (See Chapter 7.)

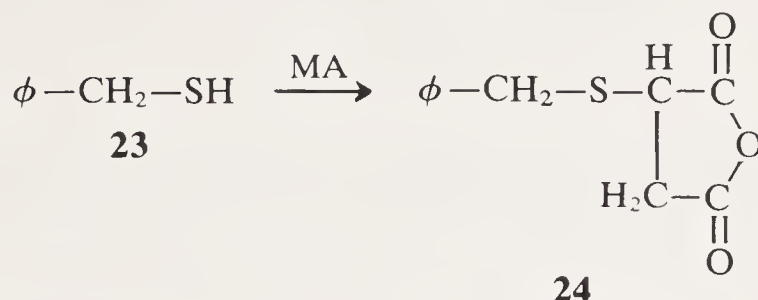


Derivatives of aspartic acid have been envisaged for application in the preparation of dyes, tanning agents, or textile assistants.<sup>(34)</sup> Their rust-inhibiting action makes them potential additives for lubricating oils and gasoline and applications such as gasoline deicing additives and detergents<sup>(42)</sup> have been proposed. Liu *et al.*<sup>(43,44)</sup> have examined aspartic acid derivatives as hypocholesteremics.

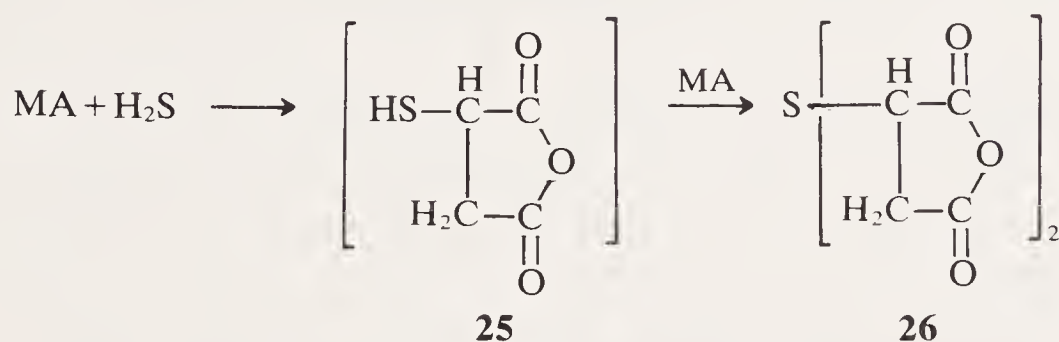
### 3.2.6. Addition of Sulfur Compounds

MA and its derivatives react readily with thiols to yield addition products. A number of sulfur compounds have been examined and many additions involving apparently complex molecules can be rationalized in terms of the addition of the S-H bond or S anion. In many cases studied, nucleophilic addition appears to be the mode of reaction. The yields, as we shall see, are so high that the reaction of thiols with MA has been used to estimate relative nucleophilicities of the thiols. However, before generalizing, one should be cautioned that reactions in the absence of a catalyst<sup>(45)</sup> and with peroxide catalyst<sup>(46)</sup> have been reported.

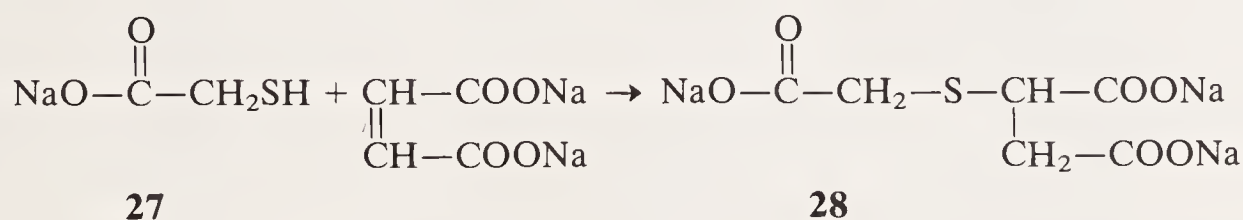
Addition of benzyl mercaptan **23** was reported by Szabo and Stiller<sup>(47)</sup> employing the triton B catalyst to yield benzylthiosuccinic anhydride **24**.



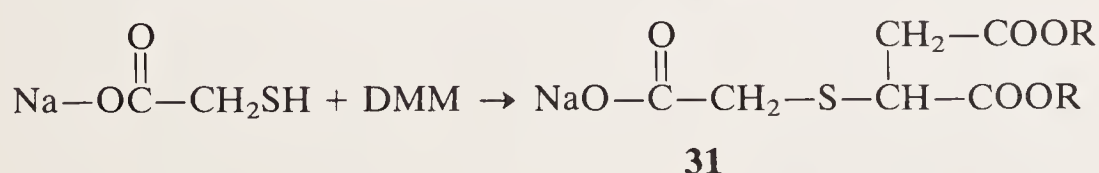
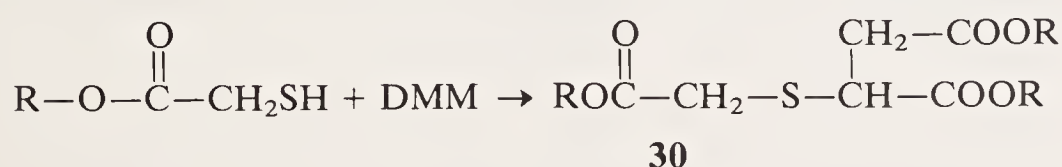
Zienty *et al.*<sup>(48)</sup> later studied the direct addition of a variety of thiols to MA using a tertiary amine as catalyst. In Table 3.3, yields of the adduct like **24** are given from that work. Apparently, even some tertiary alkyl thiols also give modest yields. Hydrogen sulfide was reported to react only in the presence of a base: A very rapid reaction occurred and no 1:1 addition product **25** was isolated. It was proposed that **25** reacted faster with MA than hydrogen sulfide to give **26**. Attempted MA reaction with H<sub>2</sub>S reportedly yielded a tarlike product following a rapid reaction.<sup>(290)</sup>



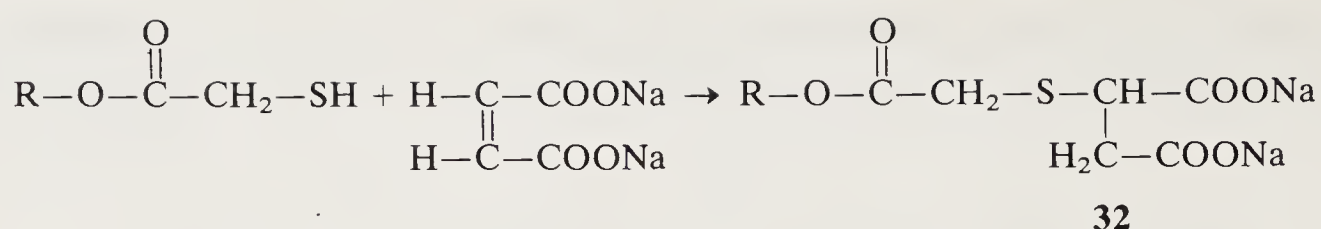
Maleic acid readily adds thiols in aqueous solutions using an alkali catalyst.<sup>(51)</sup> Esters of maleic also undergo similar addition<sup>(52,53)</sup> with sodium alcoholate or amine as a catalyst. Thioglycolic acid **27** also adds to disodium maleate giving quantitative yields of the tricarboxylic acid derivative **28**.<sup>(8)</sup>



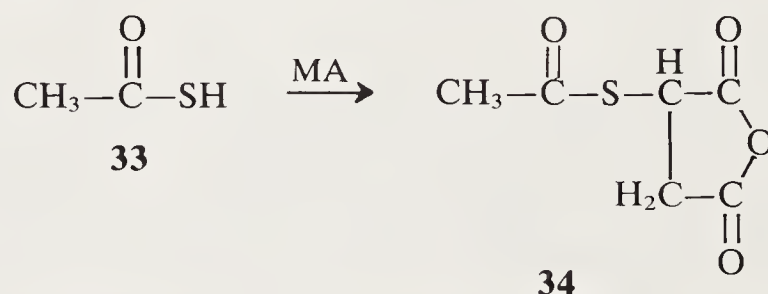
Mulvaney *et al.*<sup>(54)</sup> have prepared esters of carbomethoxymercaptop-succinic acid by employing one of the three routes shown below. This suggests the versatility possible with these compounds. (DMM = Dimethylmaleate.)





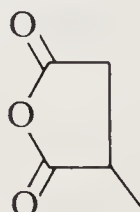


Thiolacetic acid **33** can also add to MA to give **34** in an 83% yield. Brown *et al.*<sup>(46)</sup> employed a peroxide catalyst for this reaction.



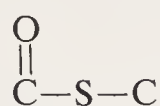
Holmberg and Schjanberg<sup>(56)</sup> have reacted **33** with maleic and fumaric acids in the absence of a catalyst. They also observe that maleic acid reacts faster than fumaric acid. Relief of repulsion of carboxyl groups in the former was suggested as the basis of its higher reactivity.

Table 3.3. *dl*-Alkylthio- and Arylthiosuccinic Anhydrides<sup>a</sup>

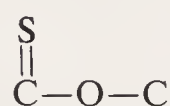
R	Melting point or boiling point (mm) °C	Yield %
CH <sub>3</sub>	142 (2)	64
<i>n</i> -C <sub>4</sub> H <sub>9</sub>	122–124 (0.3)	89
<i>tert</i> -C <sub>4</sub> H <sub>9</sub>	83.5–84.5	41
<i>n</i> -C <sub>6</sub> H <sub>17</sub>	175–179 (0.6)	89
<i>n</i> -C <sub>12</sub> H <sub>25</sub>	42–43	94
<i>tert</i> -C <sub>12</sub> H <sub>25</sub>	160–170 (0.01)	60
–CH <sub>2</sub> CH <sub>2</sub> –	128–130	42
C <sub>2</sub> H <sub>5</sub> OOCCH <sub>2</sub>	140–145 (0.2)	76
HOOCCH <sub>2</sub>	—	100
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> –	150–155 (0.03)	88
C <sub>6</sub> H <sub>5</sub> –	176–178 (1.5)	88
<i>p</i> -CH <sub>3</sub> C <sub>5</sub> H <sub>4</sub> –	155–160 (0.01)	65
<i>p</i> -ClC <sub>6</sub> H <sub>4</sub> –	96–98	97
<i>p</i> -CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> –	—	45
<i>p</i> -AcNHC <sub>6</sub> H <sub>4</sub> –	186–188	77
<i>p</i> -O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> –	114–115	90
<i>o</i> -O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> –	124–125	96
C <sub>6</sub> Cl <sub>5</sub> –	166–168	87
	—	90

<sup>a</sup> From Reference 48.

Note that the bond formed from **33** with MA and the acids is

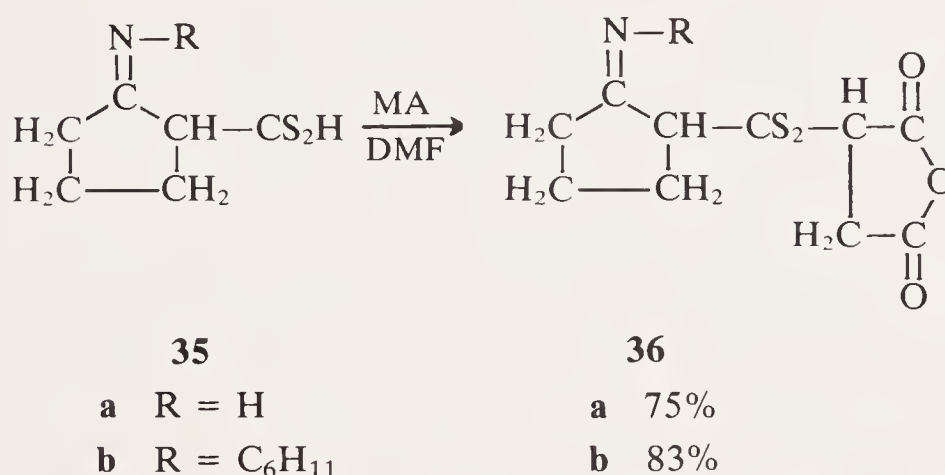


and not

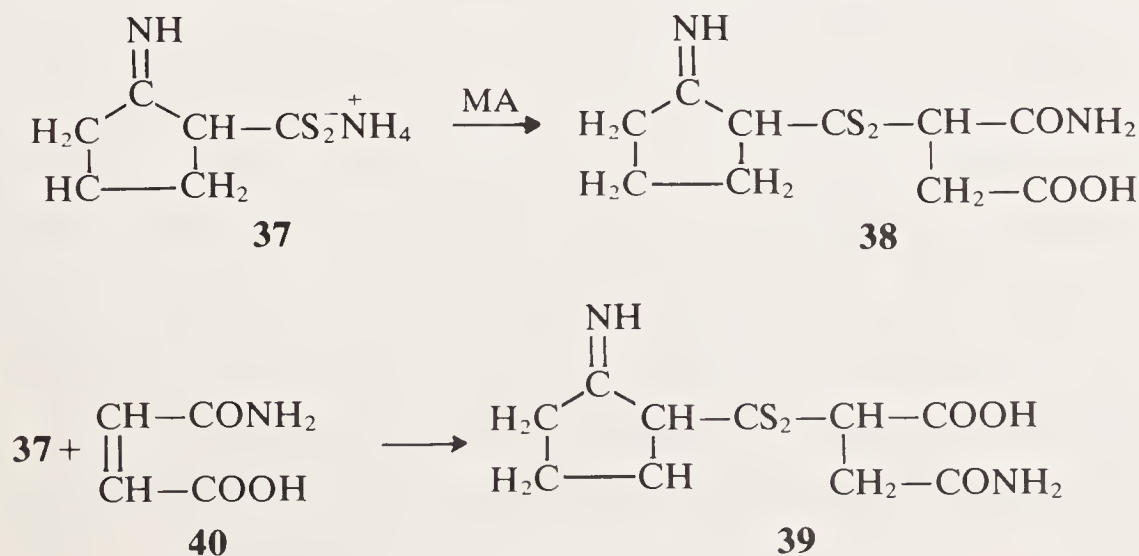


Under these conditions, the elements of acetic acid do not add across MA. This clearly reflects the relative reactivity of the SH versus the OH function.

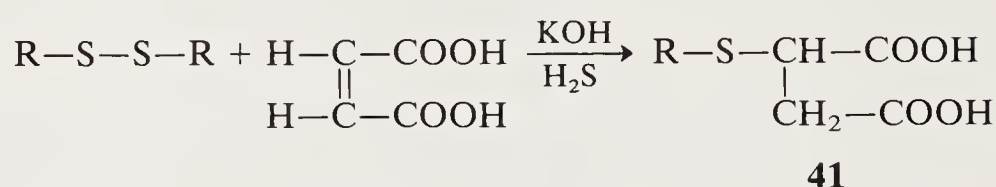
Recently, thiocarboxylic acids and their salts have been reported by Tokashima *et al.*<sup>(57)</sup> to add to MA. Thus, 2-iminocyclopentanedithiocarboxylic acid **35a** and 2-cyclohexyliminocyclopentanedithiocarboxylic acid **35b** gave 75% and 83% yields, respectively, of the adducts **36**. Maleimide, maleic diamide, and esters were all shown to undergo the reaction under very mild conditions.



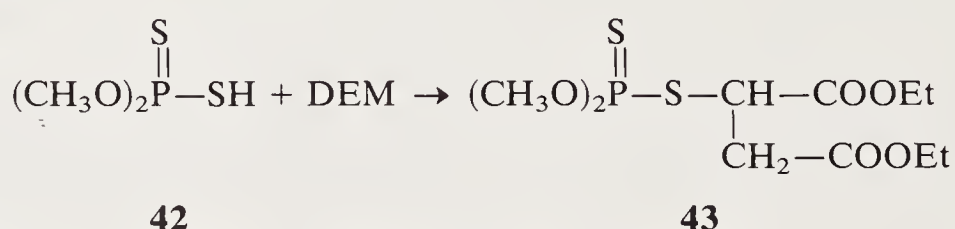
When the ammonium salt of the dithiocarboxylic acid **37** was employed, the corresponding succinamic acid **38** was formed in a 70% yield. The isomeric succinic acid derivative **39** was made by the reaction of maleamic acid **40**. During the reaction of the ammonium salt, therefore, it was believed that the addition across the double bond preceded the ammonolysis.



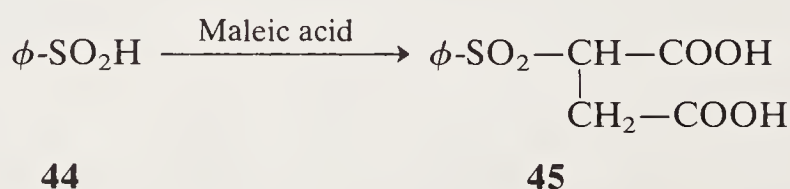
Alkylthiosuccinic acid **41** can also be prepared from the reaction of dialkyldisulfides and maleic acid in the presence of KOH and potassium sulfide.<sup>(58)</sup>



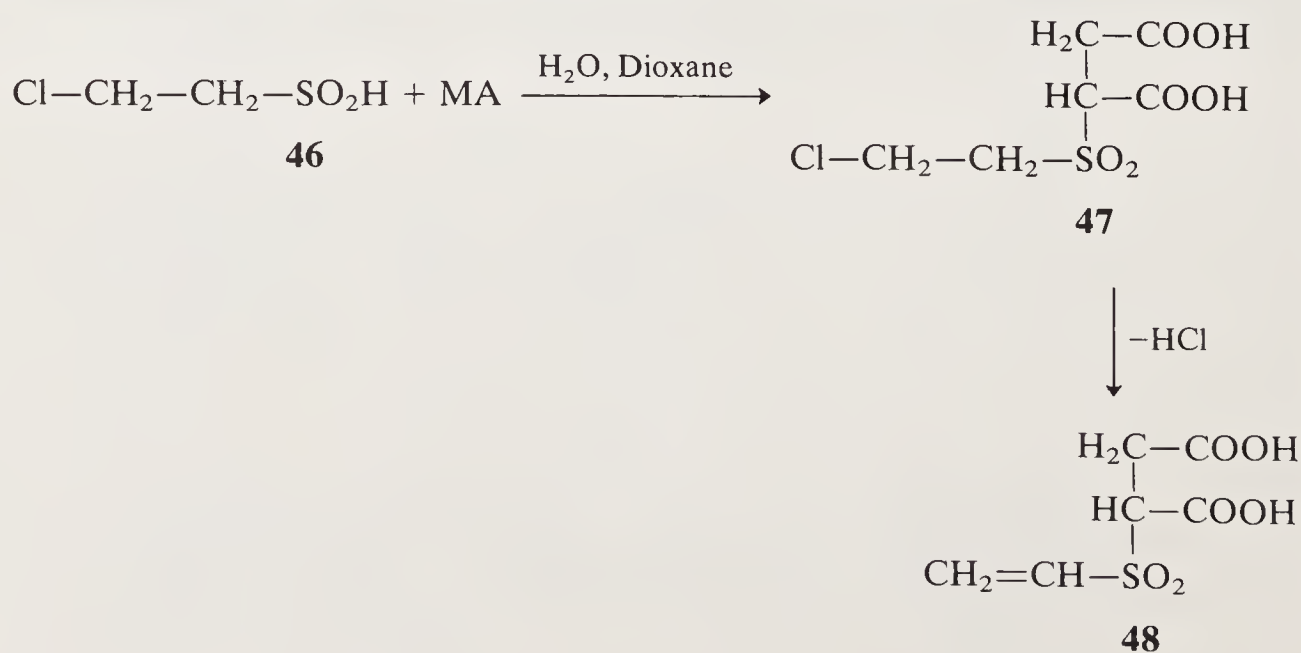
The nucleophilicity of thiols is also demonstrated in compounds containing the P-S bond. For example, Malathion<sup>R</sup> **43**, the popular insecticide, is commercially made from diethyl maleate and dimethylphosphorodithioate **42**.<sup>(68)</sup>



Compounds with higher oxidation states of sulfur also add to the unsaturation in maleic derivatives. Benzenesulfinic acid **44** adds to maleic acid in aqueous solution.<sup>(60)</sup> The insoluble acid adduct **45** is recovered in quantitative yield.

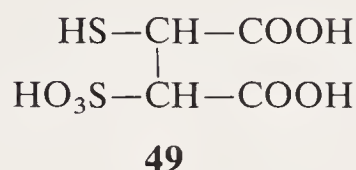


Etienne and Lonchmbon<sup>(63)</sup> have reported the addition of 2-chloroethanesulfinic acid **46** to maleic acid. In this work, the final product **47** was treated with a base to remove the elements of HCl. This afforded an interesting monomer **48**. No data on yields were given by the authors.



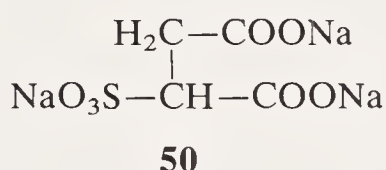


Thiosulfate has been reported to add to maleic acid to give **49**, as shown below<sup>(61)</sup>:



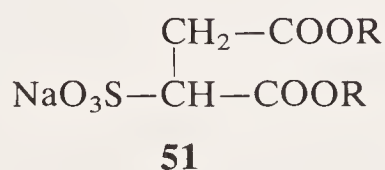
Compound **49** is interesting because it can be a precursor to disulfosuccinic acid by further oxidation. No yields were indicated; however, the formation of a significant amount of fumaric acid was reported.<sup>(62)</sup>

When maleic acid, esters, etc., are treated with sodium sulfite or bisulfite, an addition product is formed. Thus, when maleic acid sodium salt is treated with sodium bisulfite, trisodium sulfosuccinate is formed **50**.<sup>(64,68)</sup>



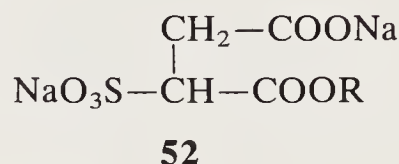
Fumaric acid can be similarly treated but it reacts less readily than maleic acid. Sulfosuccinate can also be prepared by nucleophilic displacement on bromo or chlorosuccinic acid. However, the ease of addition across the maleic derivatives has made direct addition the method of choice.

One of the interesting outcomes of this chemistry are the esters of sulfosuccinic acid. Jaeger<sup>(65)</sup> prepared them as follows: maleic anhydride was first treated with two moles of alcohol (see Sec. 3.4.3) to form the diester. On treating the dialkyl maleate with aqueous sodium bisulfite, sodium dialkyl-sulfosuccinate **51** was obtained.



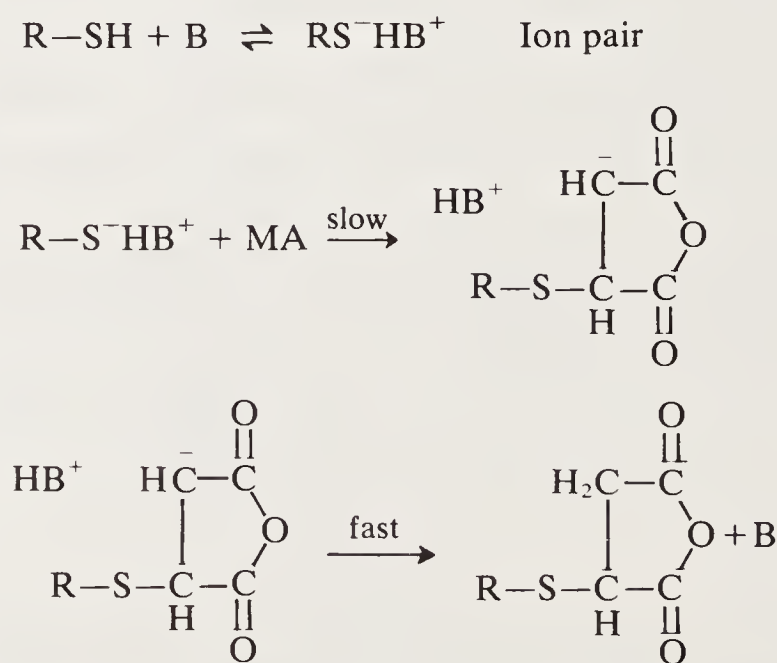
Some of these dialkyl sulfosuccinates were first commercialized by American Cyanamid under the name Aerosol surfactants. They are among the most powerful wetting agents known. The most widely known among them is dioctyl sulfosuccinate (where octyl is actually 2-ethylhexyl) which is supplied by a number of manufacturers as a wetting agent and textile auxiliary.<sup>(31)</sup> In addition, the advent of sulfosuccinate has contributed greatly toward understanding of the wetting and surface activity phenomena.<sup>(65)</sup> Caryl<sup>(66,67)</sup> has examined the wetting action of a number of these products. Since the alkyl group R can be varied at will, the reaction avails itself to custom design of a surfactant.

The half ester of maleic acid also may be treated similarly with sodium sulfite, thus giving a dianionic compound **52**.

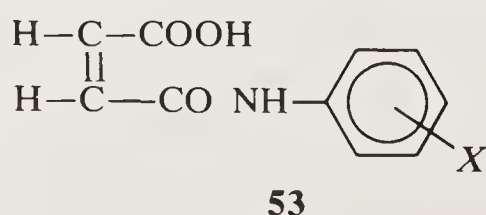


Here a variety of R groups have been used commercially. Some representative R groups include alkyl, perfluoroalkyl, and polyalkenoxyalkyl.<sup>(31)</sup>

Dmuchovsky and coworkers<sup>(49,50)</sup> have examined the kinetics of the base-catalyzed addition of thiols to MA. An overall third-order kinetics was observed—first order in each reactant and the catalyst. By the use of spectroscopic measurements, they observed an interaction between the thiol and the catalyst (triethylenediamine), but not between the thiol and MA. Solution of any one or any pair of reactants showed no electrical conductivity, suggesting insignificant concentration of free ions in solution. Furthermore, the kinetic isotope effect was determined for butanethiol, MA, and the amine catalyst. It was suggested that cleavage of the hydrogen bond is not important in the transition state. It was also shown later by Dmuchovsky and coworkers<sup>(50)</sup> that a good correlation is obtained between the  $pK_a$  of the thiols and their reactivity. Based on these evidences the following mechanistic scheme was proposed:\*



Tanchuk and Kornienko<sup>(55)</sup> have recently reported a kinetic study of the nucleophilic addition of decanethiol to various maleanilic acids **53**. A third-



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order overall rate was observed only under a certain concentration of triethylamine catalyst. Above this concentration the linear dependence of the pseudo-second-order rate constant stops (Fig. 3-1). No comments were offered as to what extent the acidity of **53** affected this observation.

It may be further added that Brown<sup>(46)</sup> employed peroxide as an initiator in the reaction of MA with thiolacetic acid as mentioned earlier. Its necessity was not explored and may be unnecessary in that particular case. Dmuchovsky and coworkers have also shown that added radical inhibitor has no effect on the rate of thiol disappearance.<sup>(50)</sup> Since the peroxide-catalyzed addition of thiol to olefin is known, only its contribution in relatively facile nucleophilic addition processes is questioned.

Addition of other sulfur compounds has been rationalized in terms of the nucleophilic attack by the sulfur center.

Alkylmercaptosuccinic acids and anhydrides are suggested as intermediates for plasticizers and resins. The ease of the reaction of this function with the unsaturation in maleic derivatives provides a possibility of crosslinking and grafting of MA-based polymers.

Surfactant and wetting properties of dialkyl sulfosuccinates were mentioned. These are variously utilized as textile auxiliaries and wetting agents for textiles and papers. The monoalkyl sulfosuccinates are also available commercially. These are used as emulsifiers for cosmetics, depilatories, wetting agents, rug shampoo additives, and in emulsion polymerization.<sup>(31)</sup> Again, since MA can be used in the reactions with any alcohol, it is possible to design a surfactant of choice. Sulfosuccinic acid was first prepared in 1927 and has seen some renewed interest as a detergent builder.<sup>(31)</sup> Sulfosuccinates have also been suggested for applications in desulfurizing coal,<sup>(291)</sup> ore beneficiation,<sup>(292)</sup> and as an antifouling agent for petroleum equipment.<sup>(293)</sup>

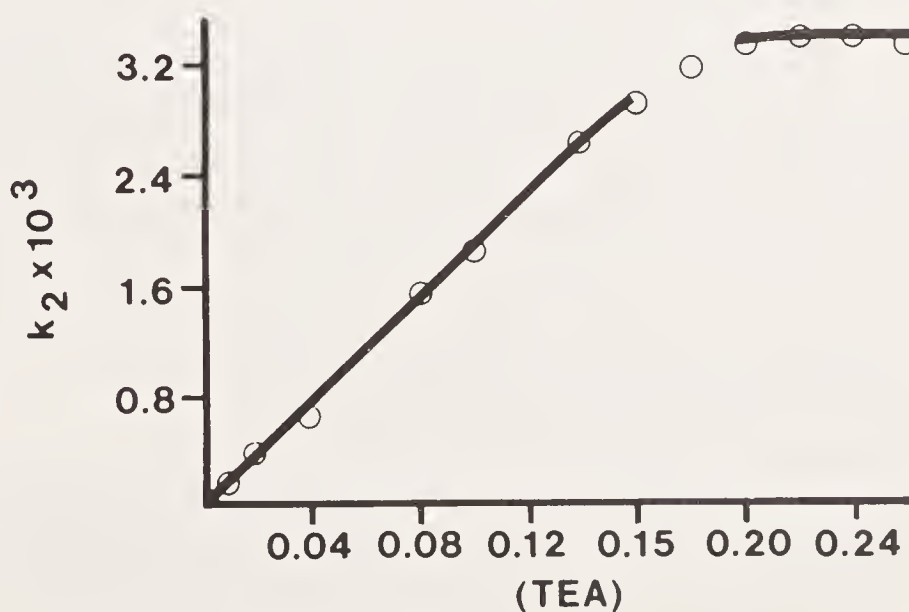
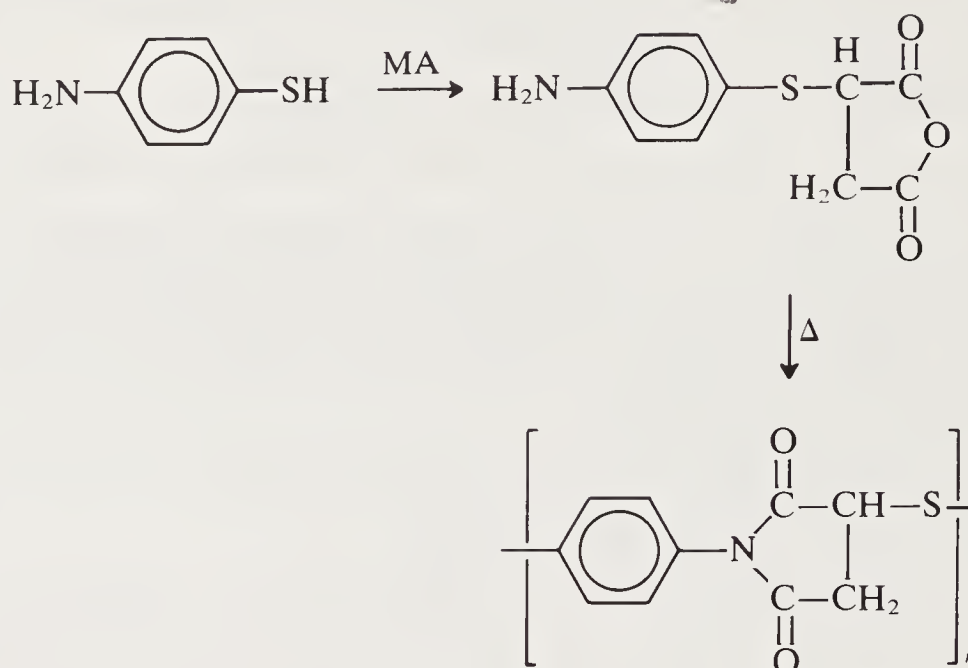


Fig. 3-1. Dependence of the constant  $k_2$  (liter/mols) on the concentration of triethylamine ( $M$ ). From Reference 55.



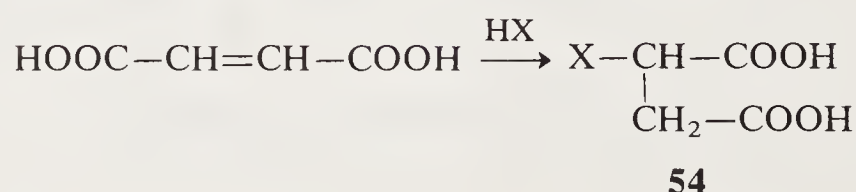
Asahara<sup>(59)</sup> has utilized the reaction of thiols with MA to form an interesting polyimide as follows:



Similarly, *p*-hydroxythiophenol forms the adduct in a 91% yield. The latter is a precursor to polyester resins.<sup>(274)</sup>

### 3.2.7. Addition of Hydrogen Halides

Halosuccinic acids (chloro and bromo) can be prepared by the addition of the elements of hydrohalic acid to the double bond:

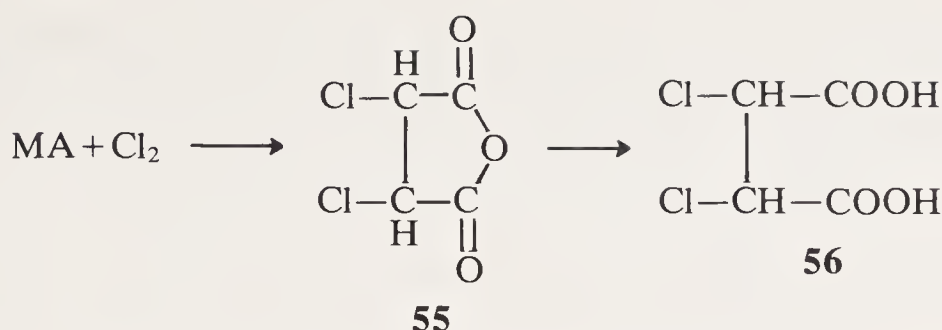


Chlorosuccinic acid **54** (X = Cl) is prepared by heating a mixture of fumaric acid and acetic acid saturated with hydrochloric acid.<sup>(25,69)</sup> Bromosuccinic acid **54** (X = Br) can similarly be prepared by treating fumaric acid with hydrogen bromide.<sup>(70)</sup>

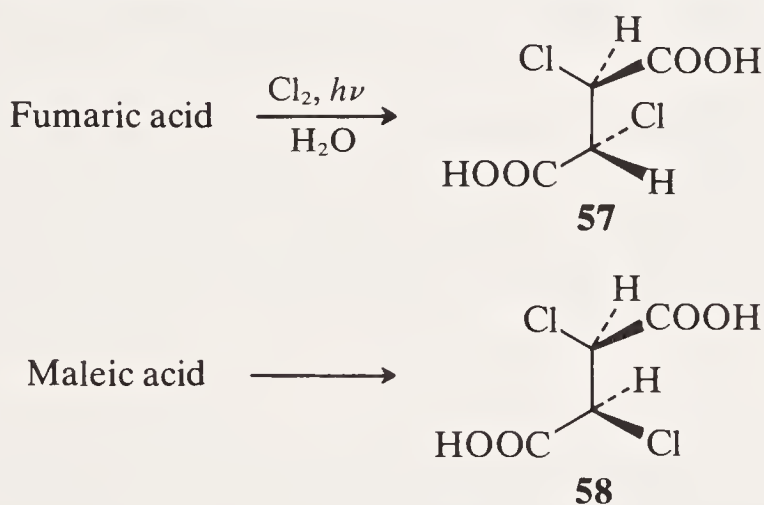
These haloacids have not found any major industrial use. As can be seen, a racemic mixture results from the synthesis. The primary use has been as an intermediate for synthesis. Those derivatives of MA that can not be easily produced by nucleophilic addition may be achieved by nucleophilic substitution on these halosuccinic acids.

### 3.2.8. Addition of Halogens

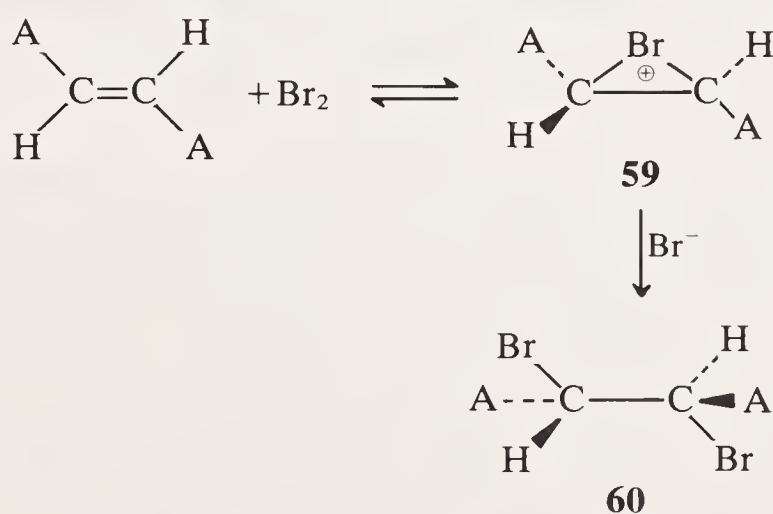
Chlorination of molten maleic anhydride yields  $\alpha,\beta$ -dichlorosuccinic anhydride **55**. Hydrolysis of the latter can yield the di-acid **56**. The addition reaction is usually carried out under pressure.<sup>(71)</sup>



Alternately, when a mixture of fumaric acid, water, and chlorine are subjected to sunlight for 4 days, a quantitative yield of the *meso* dichlorosuccinic acid **57** is obtained.<sup>(72,73)</sup> Maleic acid on the other hand gives racemic (*dl*) acid **58**. Thus, under these reaction conditions, *trans* addition is said to occur. However, if chlorine is added to soluble neutral salts of the acids in water in the presence of excess chloride ion, *cis* addition occurs.

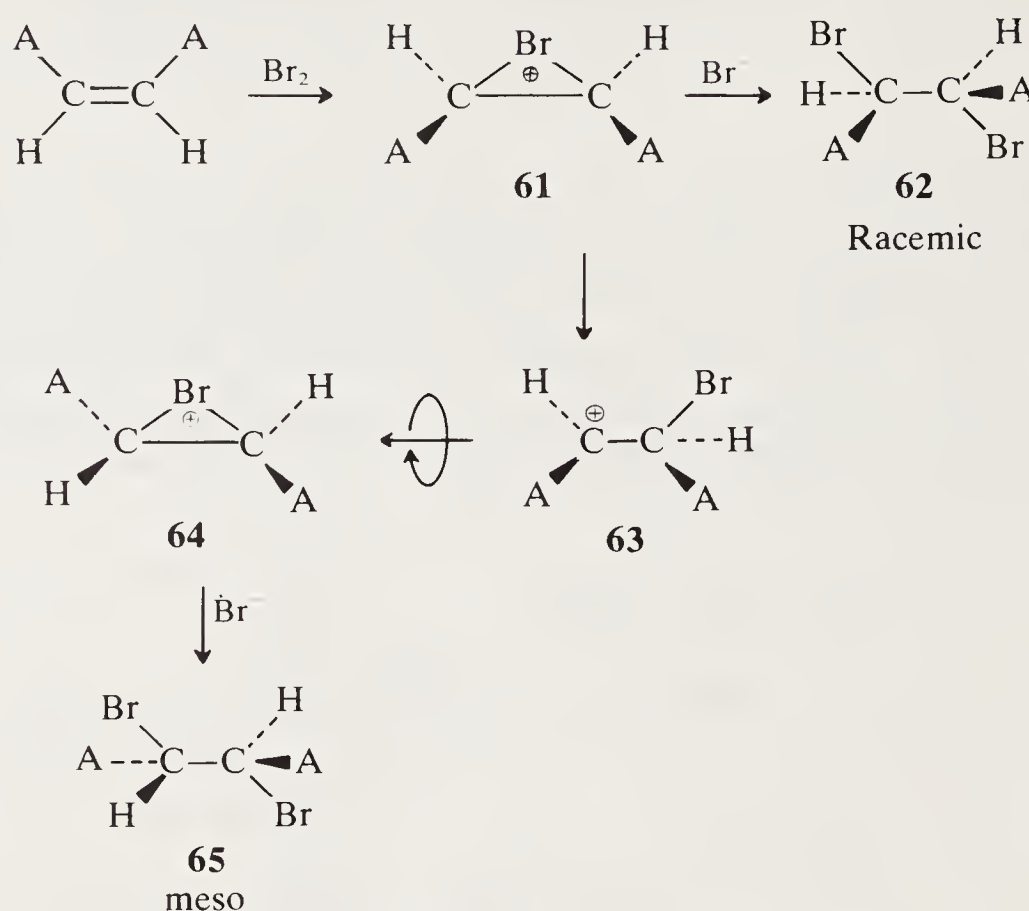


Addition of bromine has been the subject of a number of studies. When a neutral salt of maleic or fumaric acid ( $\text{A} = \text{COO}^-$ ) is brominated in water, the *meso* derivative is the predominant product.<sup>(74,275)</sup> Bell and Pring<sup>(75)</sup> also report that the *meso* product is obtained on bromination of the diethyl esters of fumaric and maleic acids. Terry and Eicheberger<sup>(76)</sup> observed 78% *meso* product from disodium maleate, a *cis* addition product which is unexpected. The prevalent bromonium ion mechanism proposed by Roberts and Kimball<sup>(77)</sup> could easily explain the *trans* addition as follows:



Thus, normal halogen addition occurs with fumaric acid. The difficulty is with maleic derivatives. It had been argued by Roberts and Kimball that

although a bromonium ion intermediate is formed, ring opening occurred due to eclipsing of the two carboxylic groups, followed by rotation of the carbonium ion to yield a cyclic species which is a precursor to the *meso* product **65**.



Recently, this explanation has been questioned. Weiss<sup>(78)</sup> has reexamined the reaction of maleate anion with bromine. He argues that if the Roberts–Kimball mechanism is correct, it could be tested against the following conclusions:

- (i) If the bromonium ion intermediate **61** was formed and then it partitioned between the racemic product and the carbonium ion, the ring opening would be decreased at lower temperature. Thus more *dl* (racemic product) should be formed.
- (ii) In the bromonium ion mechanism for maleate, the attack by bromide ion gives a *trans* addition product. Thus, in the presence of excess bromide ions, the contribution of the *trans* (*dl*) product should increase.

Table 3.4 summarizes Weiss' results on the temperature effect.<sup>(78)</sup> As can be seen, a higher temperature and not a lower temperature favors the racemic product. When fumarate ion was brominated at a lower temperature, the same distribution of products was obtained. Thus, it appears that the reaction is stereoselective for the *meso* product rather than being a stereospecific *trans* addition. At a higher temperature, *trans* bromination predominates.

In Table 3.5, increased bromide concentration is shown to give more of the *meso* product. Weiss<sup>(78)</sup> also found that increasing bromide concentrations



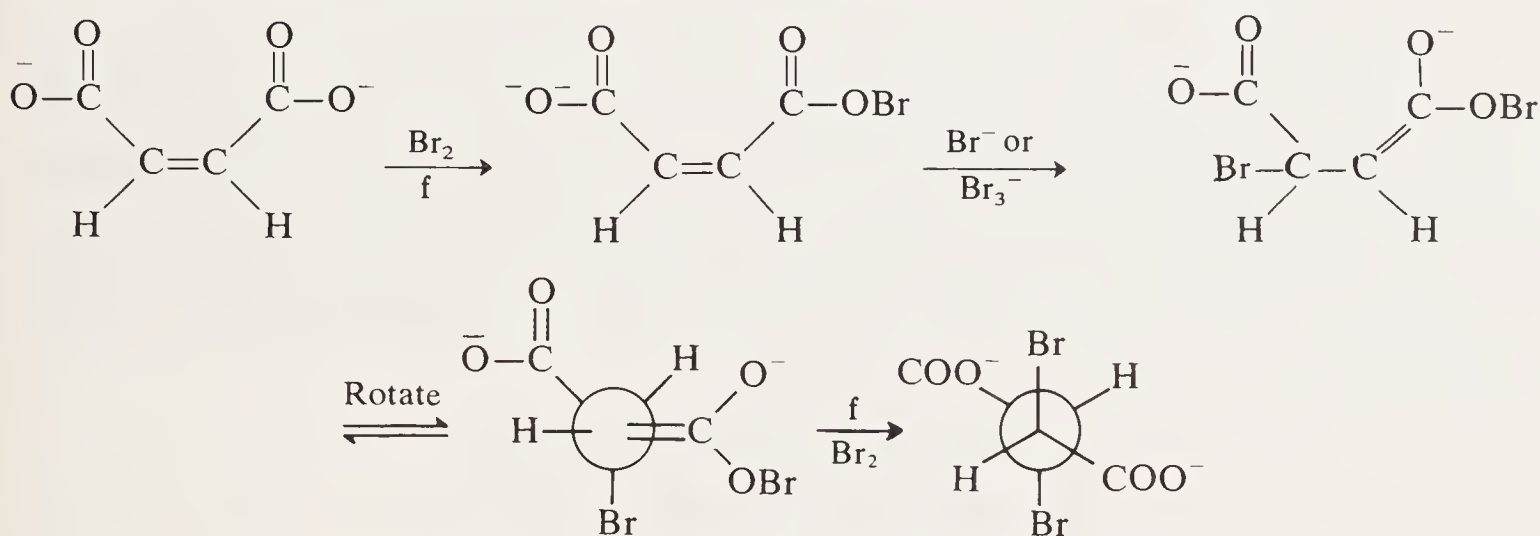
Table 3.4. Bromination of Maleate  
( $\text{Br}^-$ ) =  $0.8\text{ M}^a$

Reaction temperature ( $^{\circ}\text{C}$ )	% <i>Meso</i> product
-5	90
40	56
65	46

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failed to bring about isomerization of the maleic starting material. On allowing  $\text{Br}_2$  to be added slowly, significant isomerization did occur, suggesting that the formation of an intermediate is reversible. However, the product (dibromide) formation is rapid.

Therefore, it was proposed that there were two distinct mechanisms: One involves a higher-energy bromonium ion that is *trans* stereospecific. The other is similar to that proposed for bromination of maleic acid in acetic acid, which involves a 1,4 addition shown below, rather than a 1,2 addition.



This appears to clarify the confusion resulting from the study of product stereochemistry that has prevailed in the halogenation of maleic derivatives.

Table 3.5. Bromination of Maleate  
at  $40^{\circ}\text{C}^a$

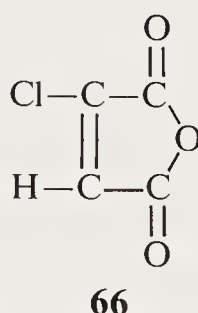
Molarity of $\text{Br}^-$	% <i>Meso</i> product
0.0	32
0.2	38
0.8	56
4.0	73

<sup>a</sup> Reprinted with permission from *J. Am. Chem. Soc.* **99**, 1670 (1977). Copyright © 1977, American Chemical Society.

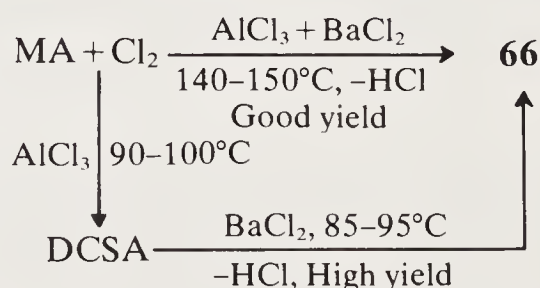
Thus, as can be seen, the halogenation of maleic acid derivatives has contributed a great deal toward understanding the stereochemical and electronic mechanism of halogenation in general. Synthetically, high yields of the products are obtained making these products attractive intermediates for a variety of uses.

### 3.2.9. Halogen Substitution

It was seen earlier that MA derivatives can add the elements of a halogen. It is also known that halogens, particularly chlorine and bromine, undergo substitution reactions as well. Thus, monochloromaleic anhydride **66** is formed when chlorine is allowed to react with MA in the presence of aluminum chloride and barium chloride.<sup>(79,80)</sup>

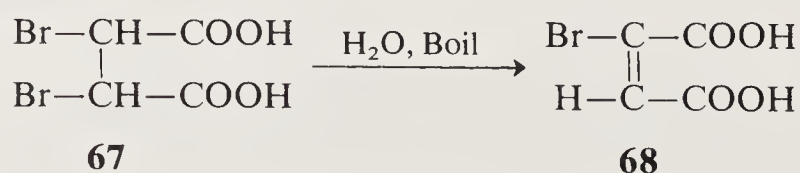


Milone<sup>(80)</sup> has shown that in the presence of aluminum chloride alone, at 90–100°C, the primary product is dichlorosuccinic anhydride (DCSA). At this stage, no significant evolution of hydrogen chloride occurred. On addition of barium chloride, a rapid evolution of hydrogen chloride occurred. Thus, it would appear that the primary reaction catalyzed by  $\text{AlCl}_3$  was the addition of chlorine and barium chloride promoted the elimination of  $\text{HCl}$  as shown in the scheme.

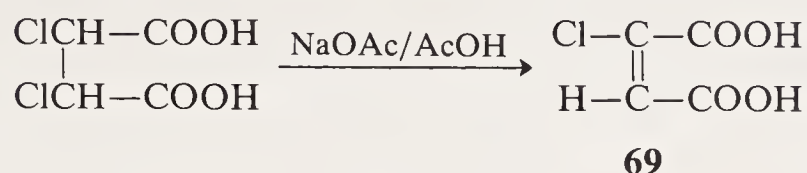


Since qualitative yields were described, it is difficult to conclude the quantitative nature of the promotions. The total reaction time in the presence of barium chloride was reported to be much shorter as well. This dual-function catalysis warrants further investigation.

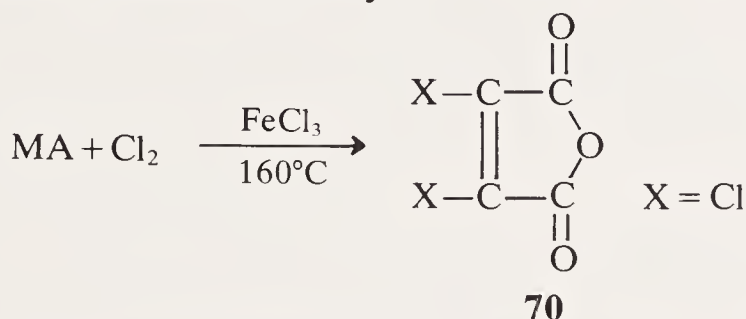
Bromination is generally accomplished in two steps. Dibromosuccinic acid **67**, obtained from bromine addition, when boiled with water yields monobromomaleic acid **68**.<sup>(71)</sup>



The ease of hydrogen halide elimination can also be used for forming chloromaleic acid<sup>(71)</sup> **69** from dichlorosuccinic acid **56**.

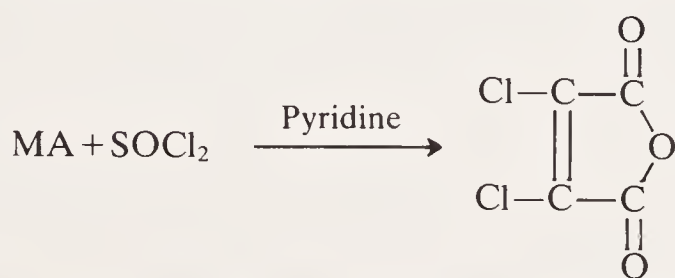


Recently, Hashizume *et al.*<sup>(83)</sup> have reported the production of dichloromaleic anhydride in very good yields by direct chlorination of MA in the presence of ferric chloride catalyst.

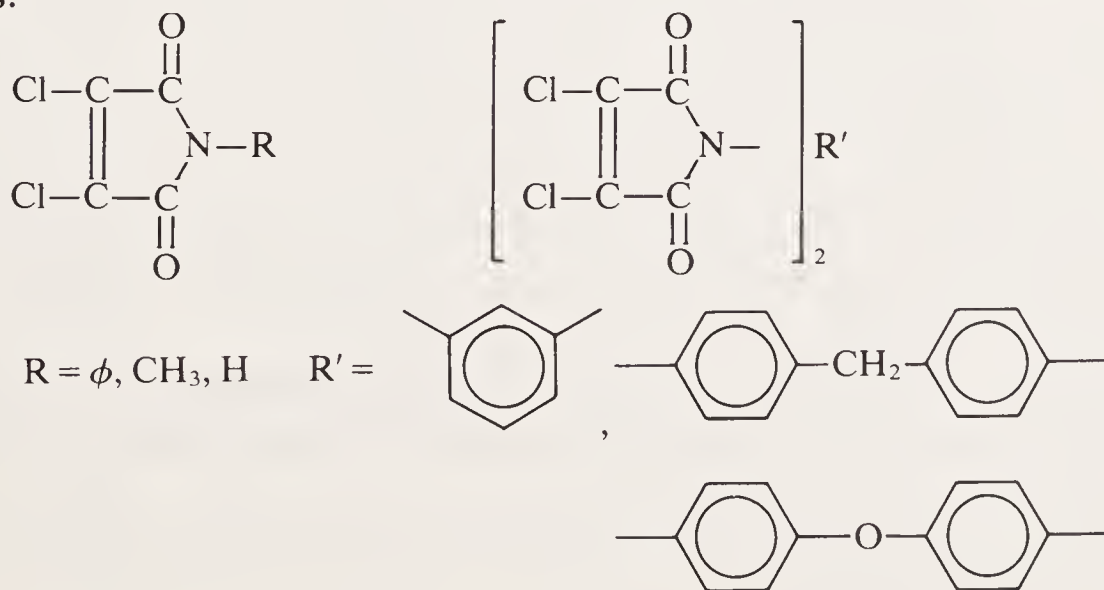


They observe<sup>(84-86)</sup> that the presence of fumaric acid, maleic acid, or water improves the yield significantly. However, the reason was not specified. A contribution by HCl formed *in situ* cannot be ruled out.

Very high yields of the dibromomaleic anhydride **70** (X = Br) have been obtained by Brown<sup>(89)</sup> using liquid-phase bromination in the presence of aluminum tribromide catalyst. It is also possible to replace both hydrogens of MA for halogens by other means. Relles,<sup>(81,82)</sup> during a study on maleimide chemistry, has shown that dichloromaleic anhydride **70** can be obtained in a 99% yield. Chlorination of MA was performed with thionylchloride/pyridine.

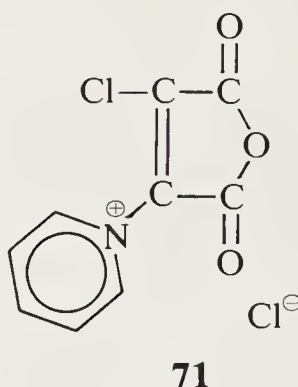


A number of maleimide derivatives shown below were also obtained in good to high yields.

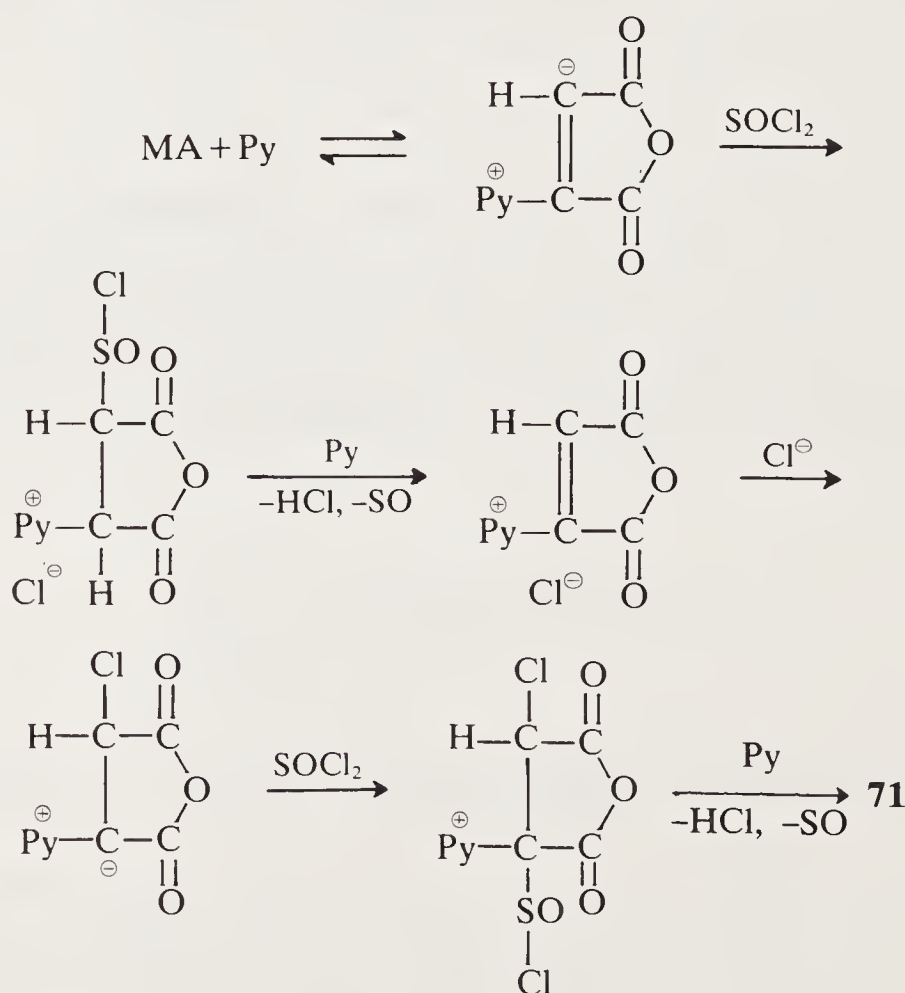




Since imide formation from halomaleic anhydride may involve side reactions, this could be an effective way to obtain these useful compounds. In an excellent study, some evidence was obtained for the presence of **71**, which was very reactive and was proposed as an intermediate.<sup>(82)</sup>



Based on the chlorination of maleimides, Relles<sup>(82)</sup> has proposed the following mechanism.\* Although the proposed mechanism involves *N*-phenylmaleimide, the same is assumed to hold true for MA. (Py = Pyridine.)



Workers at BASF<sup>(87)</sup> have also reported direct chlorination of MA with excess chlorine. In the presence of amide catalysts the product was polychloropropionyl chloride.

Halogenation, particularly chlorination, gives different products depending on the catalyst. In most cases, the yields are high, giving a useful variation.

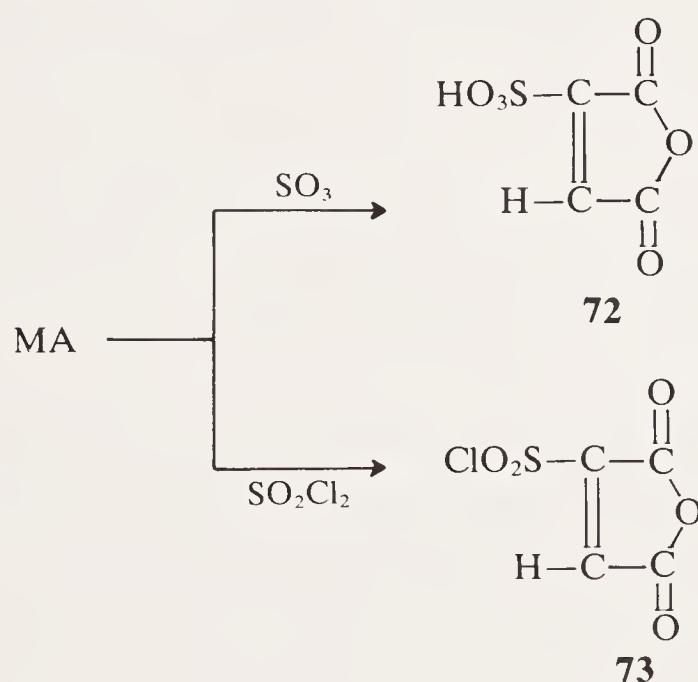
\* Reprinted with permission from *J. Org. Chem.*, **37**, 3630 (1972). Copyright © 1972, the American Chemical Society.

Since different MA derivatives can be utilized, a variety of options can be employed for optimum results.

These products are valuable intermediates for insecticides, herbicides, etc.<sup>(25,87,88)</sup> Monochloro **66**, dichloro **70** ( $X = \text{Cl}$ ), and dibromo **70** ( $X = \text{Br}$ ) derivatives are useful monomers in their own right for fire-resistant coatings, textiles, and plastics.<sup>(25,89)</sup>

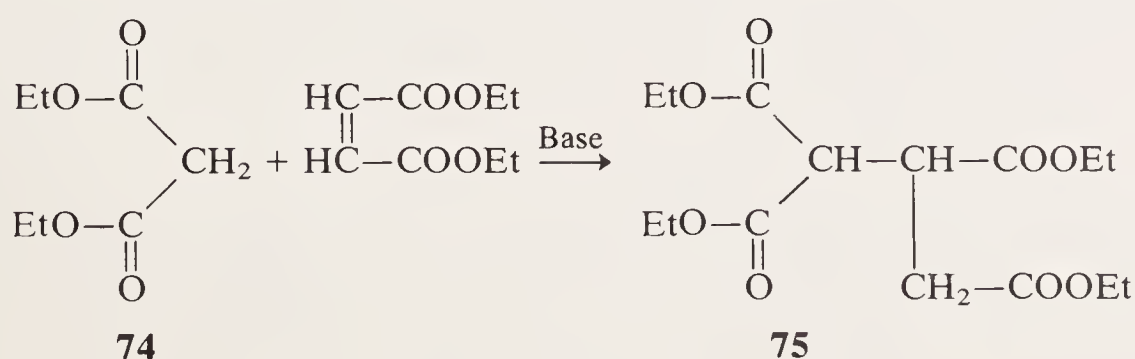
### 3.2.10. Sulfonation

Direct sulfonation of MA with sulfur trioxide to give sulfomaleic anhydride **72** and chlorosulfonation to yield chlorosulfonylmaleic anhydride **73** have been reported.<sup>(263)</sup> These products, due to their functionalities, could be good monomers and intermediates.

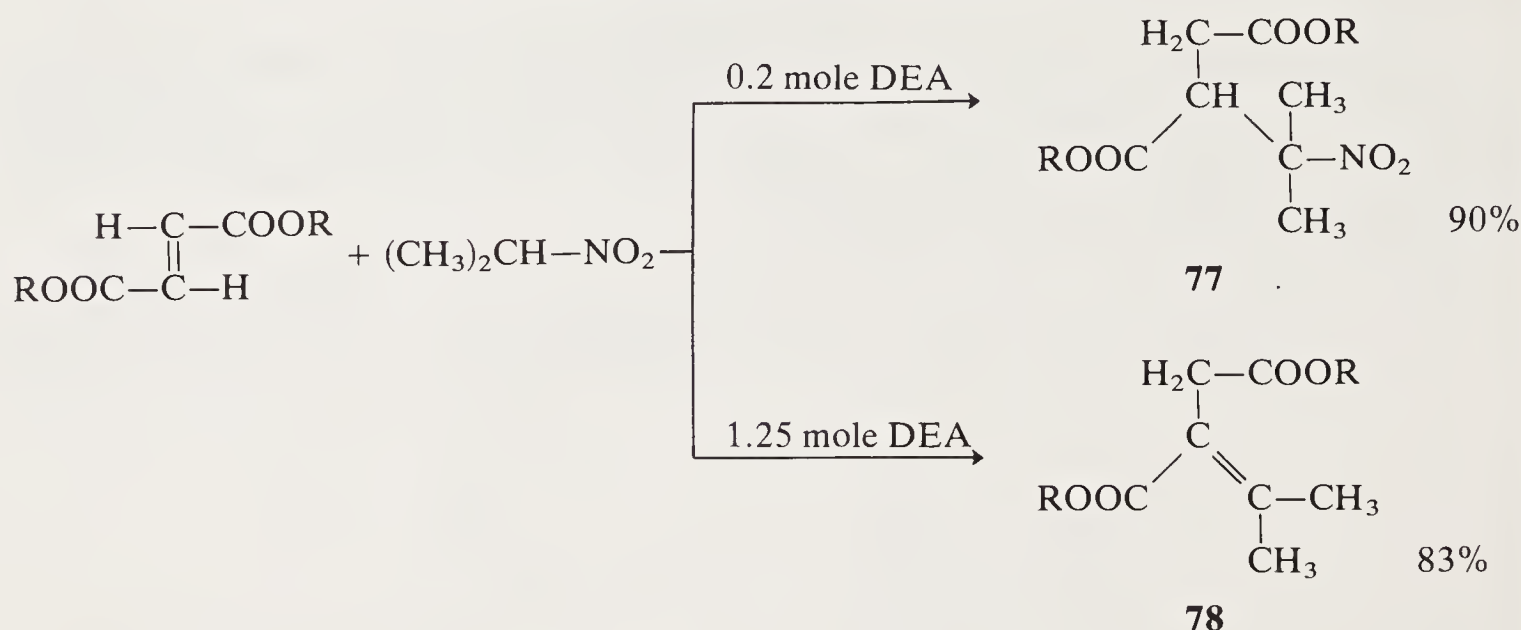


### 3.2.11. Michael Reaction: Anion Addition

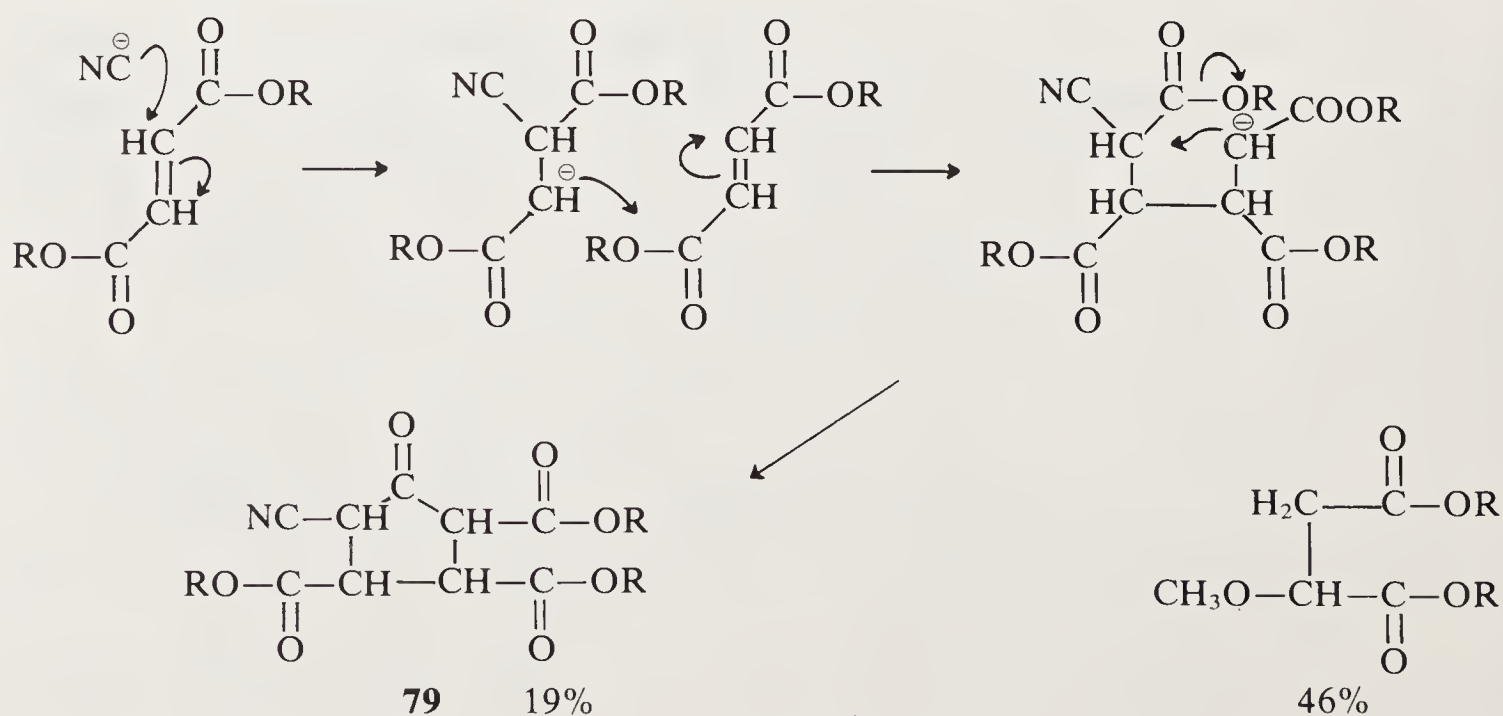
The conjugate addition of a carbanionic species across the activated double bond, such as in the esters of maleic and fumaric acid, are typical examples of Michael addition. Carbanions are usually generated using a base catalyst and, hence, reaction of MA itself has not been attempted. A representative example of the addition of diethyl malonate **74** to diethyl maleate, which produces the tetracarboxylic ester **75**, is shown below.<sup>(90,91,98)</sup>



A number of reactants that can give rise to anionic species have been used. These include esters of phenylacetic acid,<sup>(92)</sup> malonic and alkylmalonic acids,<sup>(93,94)</sup> acetoacetic acid,<sup>(95)</sup> etc. Also useful are some nitriles and nitroalkanes.<sup>(96)</sup> The case of 2-nitropropane **76** is interesting. Kloetzel<sup>(97)</sup> reported that the nature of the product from diethyl fumarate depends on the amount of diethylamine (DEA) catalyst employed. Thus, using 0.20 mole of catalyst, the simple addition product **77** was formed in a 90% yield. However, with 1.25 moles of base, elimination occurred giving **78** in an 83% yield.



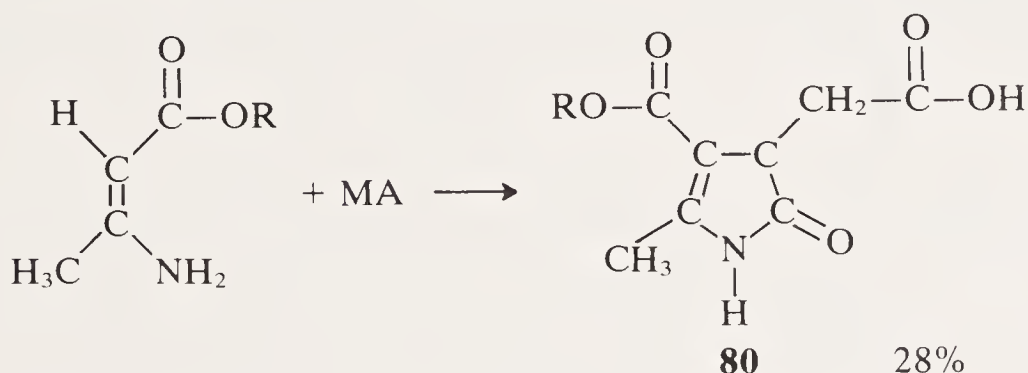
Often carbanions generated by the addition of a nucleophile to a maleic derivative can add to other molecules of the MA derivative. When this chain continues, polymerization results. In some cases, the chain may terminate to give interesting molecules. For instance, in the reaction of dimethyl fumarate with alkali cyanide, Michael and Werner<sup>(99)</sup> found **79** as the product in addition to 46% of dimethyl methoxysuccinate. The scheme below explains the product **79**. Alkoxide ion produced as a result of ring closure can also add to dimethyl fumarate to yield the methoxysuccinate derivative. In the presence of water,



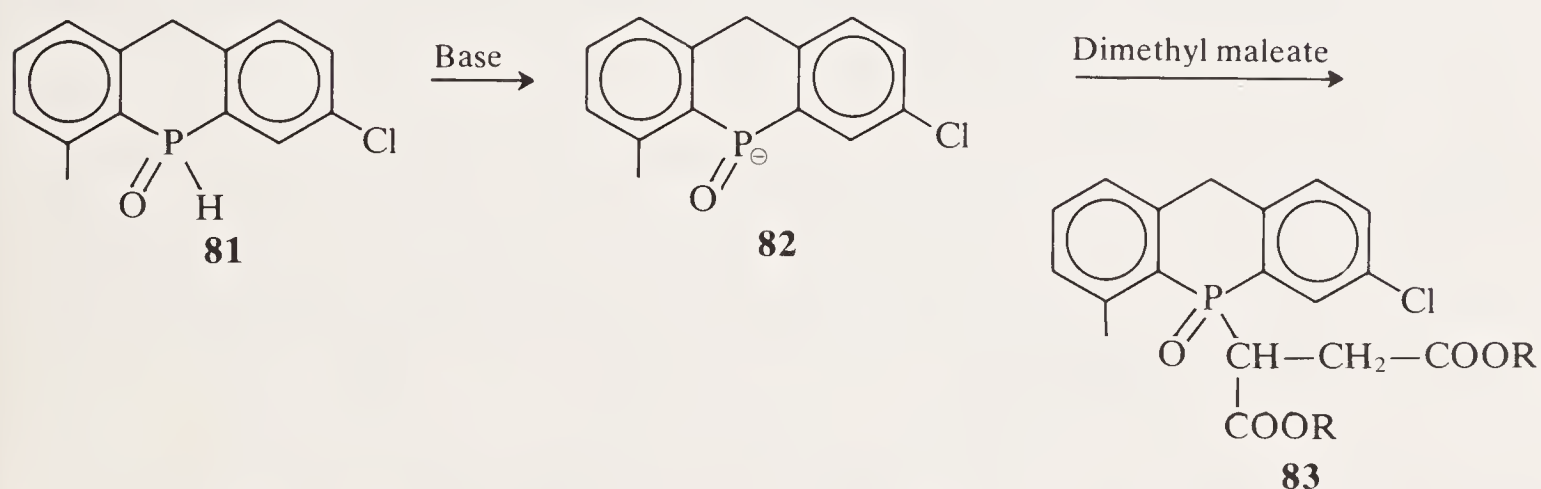


an anion precursor to **79** is protonated, suggesting it to be an intermediate in the process.

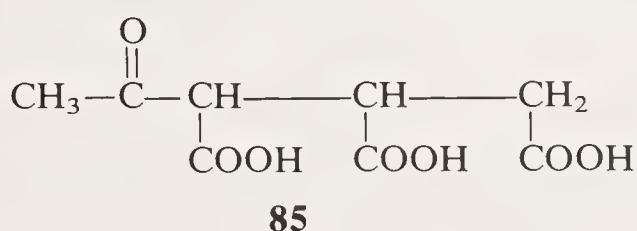
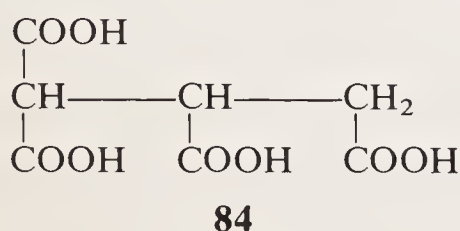
In some cases, where possible, an internal Michael reaction may lead to ring closure. A case in point is the formation of **80** from  $\beta$ -aminocrotonic acid ester and MA. Szilagyi and Wamhoff<sup>(279)</sup> reported the cyclization due to internal polarization. However, amide nitrogen shares its electrons with difficulty. It is possible that a reversible Michael addition triggered by the amine brings about the closure. Carbon-carbon bond formations due to reversible Michael reactions have been reported.<sup>(288)</sup>



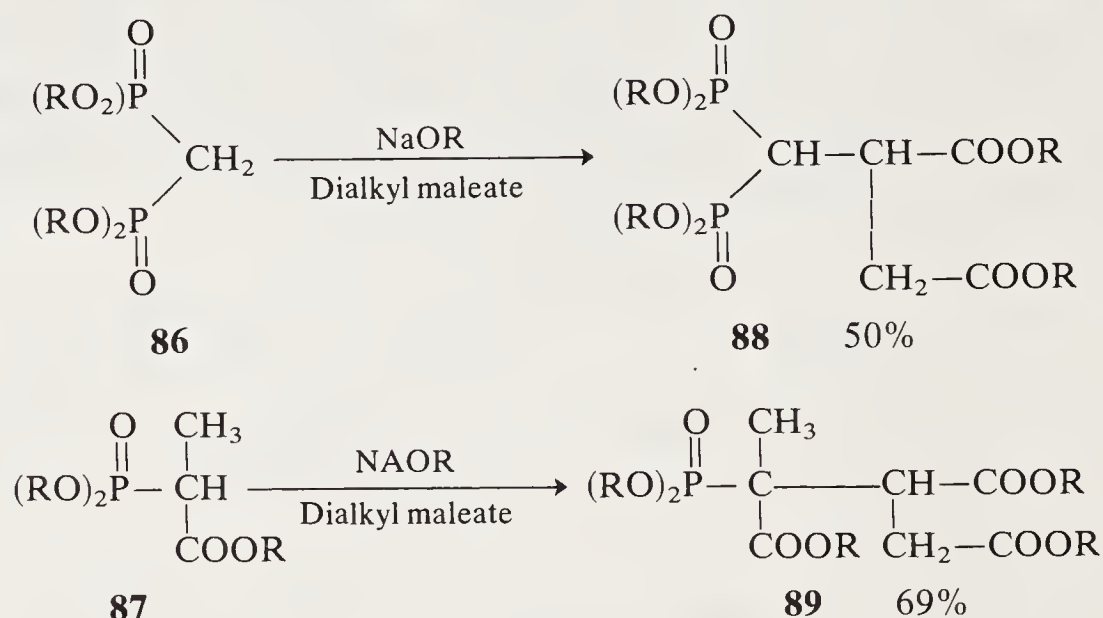
The anion may also be other than a carbanion, as exemplified by Campbell<sup>(101)</sup> in the addition of the anion **82** made from the phosphorous heterocycle **81** to dimethyl maleate. The adduct **83** was isolated as the diacid **83** (R = H).



This interesting reaction has been reviewed.<sup>(96)</sup> As is evident, maleates or fumarates can be employed as starting material and in many cases high yields of the product could be obtained. Due to the nature of the functional anion needed, the final product is usually highly functionalized. For instance, malonic acid or acetoacetic acid esters give rise to polycarboxylic acids **84** and **85**. These could be potentially useful as detergent builders. Polycarboxy functions are also useful for resins such as in the curing of epoxies.



Carbanions generated from tetraalkyl methylenediphosphonate **86** and dialkyl-1-carboxyalkylethyl phosphonate **87** add to esters of maleic acid to give the respective adducts. The hydrolysis products of **88** and **89** are claimed to be good sequestering agents.<sup>(100)</sup>

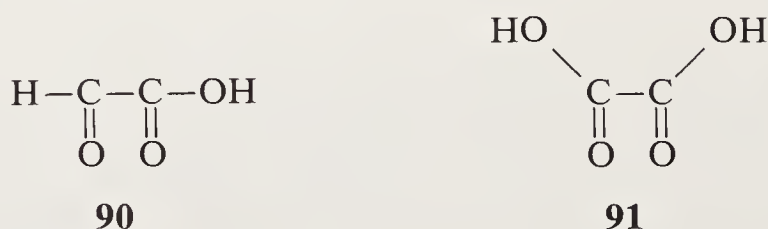


### 3.3. OXIDATION REACTIONS

The oxidation of the olefin bond in MA and its derivatives is easily achieved with a variety of reagents.

#### 3.3.1. Ozone

Ozonization of maleic acid was reported by Harries in 1903.<sup>(102)</sup> The products isolated were glyoxalic acid **90** and oxalic acid **91**. The intermediate ozonide was not mentioned.



In a related study, Noller and coworkers<sup>(103)</sup> examined ozone uptake by derivatives of MA. They observed that maleic acid and dimethyl maleate absorb less than the theoretical amount of ozone (see Fig. 3-2). Further, it was shown that the *trans* ester (i.e., fumarate) reacted much faster than the *cis* ester (i.e., maleate). This observation was based on the amount of unconsumed ozone. It is also of interest to note that dimethyl fumarate absorbed 1.7 equivalents of ozone, although no explanation or product study was made. The assumption was made that unreacted ozone did not decompose.

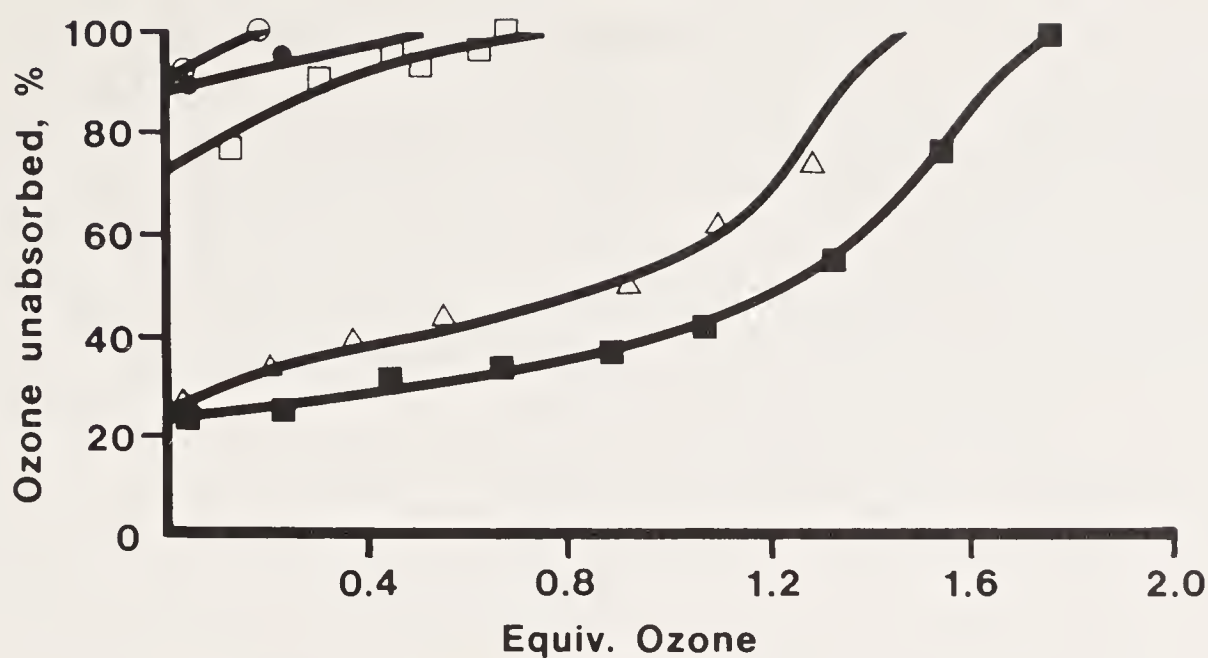


Fig. 3-2. Ozonation of unsaturated acids and esters. From Reference 103.

Briner and coworkers have also examined ozonation of maleic acid, fumaric acid,<sup>(104)</sup> and their esters.<sup>(105)</sup> Dielectric constants and Raman spectra of the ozonide of the esters are given.<sup>(105-107)</sup>

Gilbert recently examined the ozonation of maleic and fumaric acids in aqueous solution.<sup>(108)</sup> In a detailed study, he observed that the concentration of maleic and fumaric acids dropped linearly with time as determined spectrophotometrically. However, at low concentrations of maleic acid (or toward the end of the reaction) further oxidation of the primary products occurred. Maleic acid consumed 1.28 equivalents of ozone in contrast to Noller's less than theoretical amount. The primary products of reaction, namely, glyoxalic acid and formic acid, reached a maxima (Fig. 3-3) after complete consumption

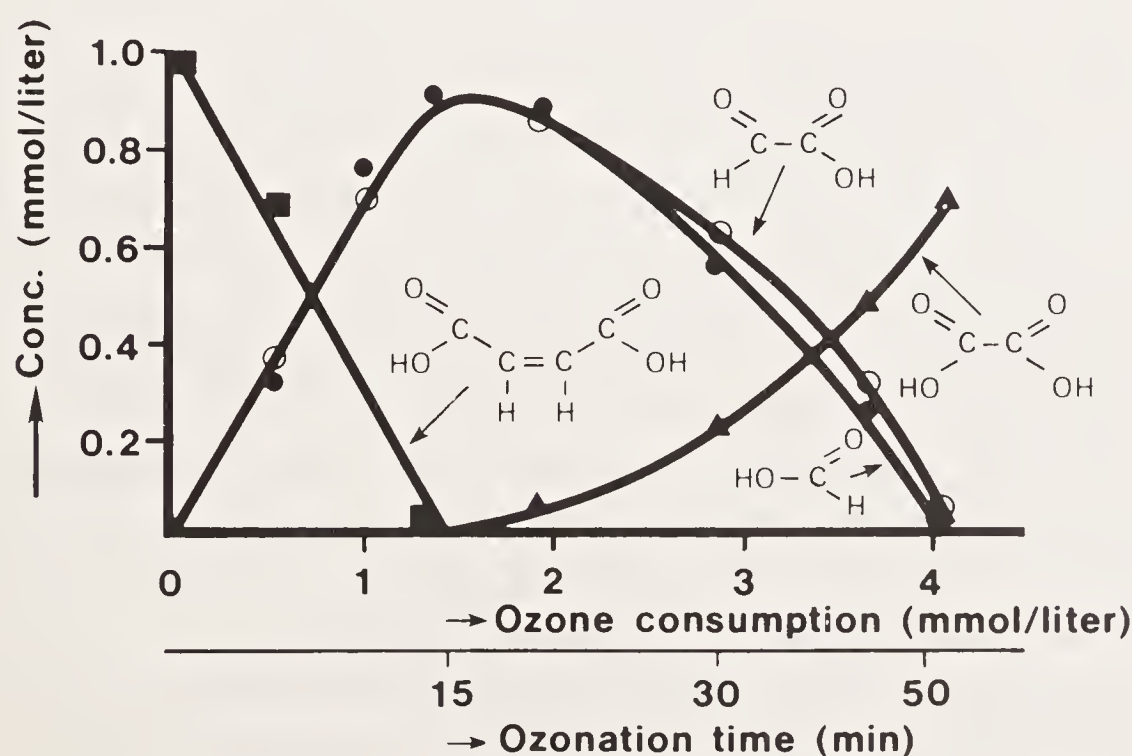


Fig. 3-3. Ozonation of maleic acid. Change in concentration in the oxidation products. From Reference 108.



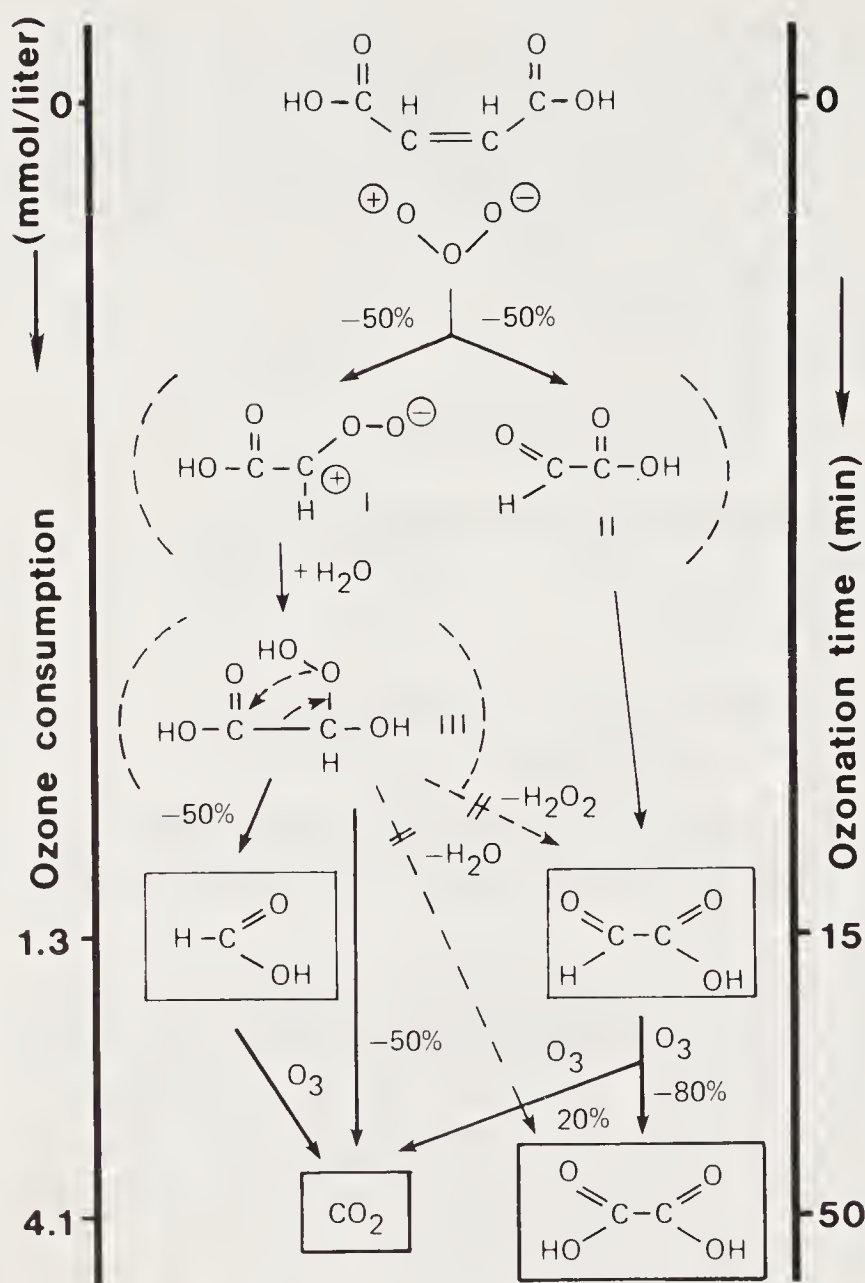


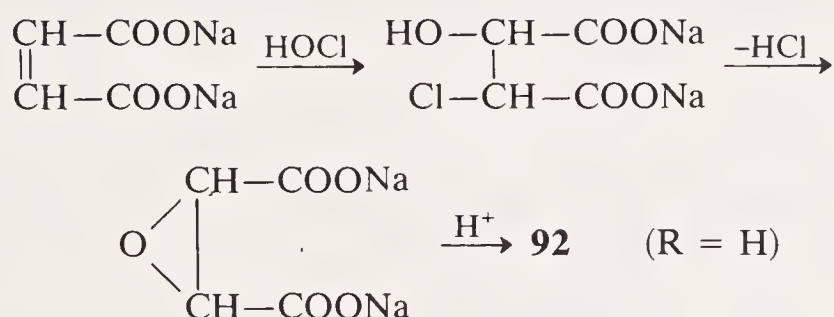
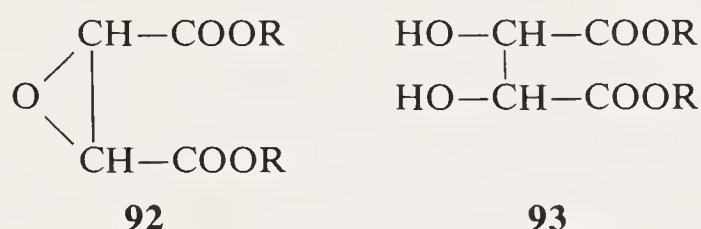
Fig. 3-4. Ozonation of maleic acid reaction scheme. From Reference 108.

of maleic acid. These further oxidized to oxalic acid and formic acid. To explain the products, Gilbert proposed the scheme in Fig. 3-4. Fumaric acid, he observed, gave two additional products: mesoxalic semialdehyde and mesoxalic acid. Yamamoto *et al.*<sup>(296)</sup> have found that the products of ozonation of maleic acid depend on the solvent. Thus, it appears that ozonation of maleic derivatives is far from simple. It is not clear why Noller *et al.*<sup>(103)</sup> observed less than theoretical ozone absorption. Furthermore, Gilbert<sup>(108)</sup> employed a sophisticated analytical procedure, unlike Noller *et al.* who determined only O<sub>3</sub> uptake versus time, and the rate of disappearance of the starting material was not followed. As mentioned, certain assumptions by Noller *et al.*, regarding concentration of O<sub>3</sub> in the stream, may not be valid.

Briner and Frank<sup>(109)</sup> studied the ozonation of maleic anhydride in chlorinated solvents. Between  $-80$  and  $-15^{\circ}\text{C}$ , MA consumed 1 mole of ozone to form an unstable ozonide. The latter caused an explosion and an injury. Thus, as with all ozonides, caution is advised.

## 3.3.2. Epoxidation and Related Reactions

The double bond in MA and derivatives can be epoxidized to yield epoxysuccinic acid derivatives **92**. So far, the primary use of this reaction has been for the synthesis of tartaric acid **93** (R = H). Epoxysuccinic acid can also be made by the hypochlorite reaction of maleic acid.<sup>(110)</sup> The final product, *dl-trans*- $\alpha,\beta$ -epoxysuccinic acid **92** (R = H) is isolated in a 75% yield.



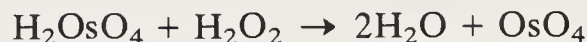
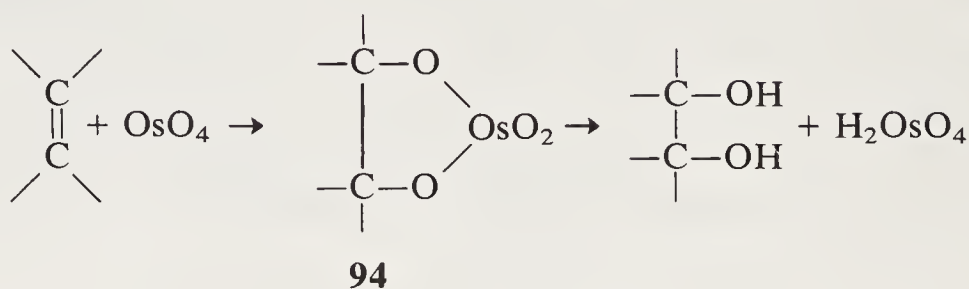
Recently, there has been renewed activity in this area. Saotome *et al.*,<sup>(111,112)</sup> Petritsch and Korl,<sup>(113)</sup> and Wagner and Schafer.<sup>(114)</sup> have used epoxysuccinic acid as an intermediate for tartaric acid **93** (R = H) synthesis. In these patent arts, epoxidation is carried out with hydrogen peroxide using the W<sup>6+</sup> catalyst. For example, Saotome *et al.*<sup>(111,112)</sup> epoxidized maleic acid in aqueous solutions at 70°C. Further heating at 102–104°C for 3 h gave a 75% *dl*-tartaric acid. Wagner and Schafer<sup>(114)</sup> and Petritsch and Korl<sup>(113)</sup> employed the Ca salt of maleic acid. Tungstic-acid-catalyzed epoxidation was reported by Wagner to give a 98% yield of calcium tartarate.

Since two optically active centers are created during the reaction, besides the *d* and *l* forms, a *meso* form is possible. This form has no residual optical activity. As was seen earlier, epoxidation of acids or salts yields a mixture of *dl* isomers. In order to synthesize the *meso*-tartaric acid, direct hydroxylation of acids or esters is employed.

The osmium-tetroxide-catalyzed oxidation of olefin is well known.<sup>(115)</sup> In the presence of another oxidizing agent such as hydrogen peroxide, Milas and Sussman<sup>(116)</sup> have investigated glycol formation from various olefins including maleic acid derivatives. In this case, using hydrogen peroxide in *tert*-butyl alcohol, maleic acid gave 30.3% yield of *meso*-tartaric acid. Fumaric acid similarly gave *dl*-tartaric acid in a 48.3% yield.

The role of osmium tetroxide in *cis* hydroxylation<sup>(115)</sup> has been established. A cyclic ester of osmic acid **94** is formed. Hydrolysis produces an Os

(VI) species that is subsequently oxidized by the oxidizing agent to the active Os (VIII) species.



When the cooxidant is hydrogen peroxide or potassium chlorate, the product is tartaric acid. Thus, Zelikoff<sup>(117)</sup> reports a quantitative yield of

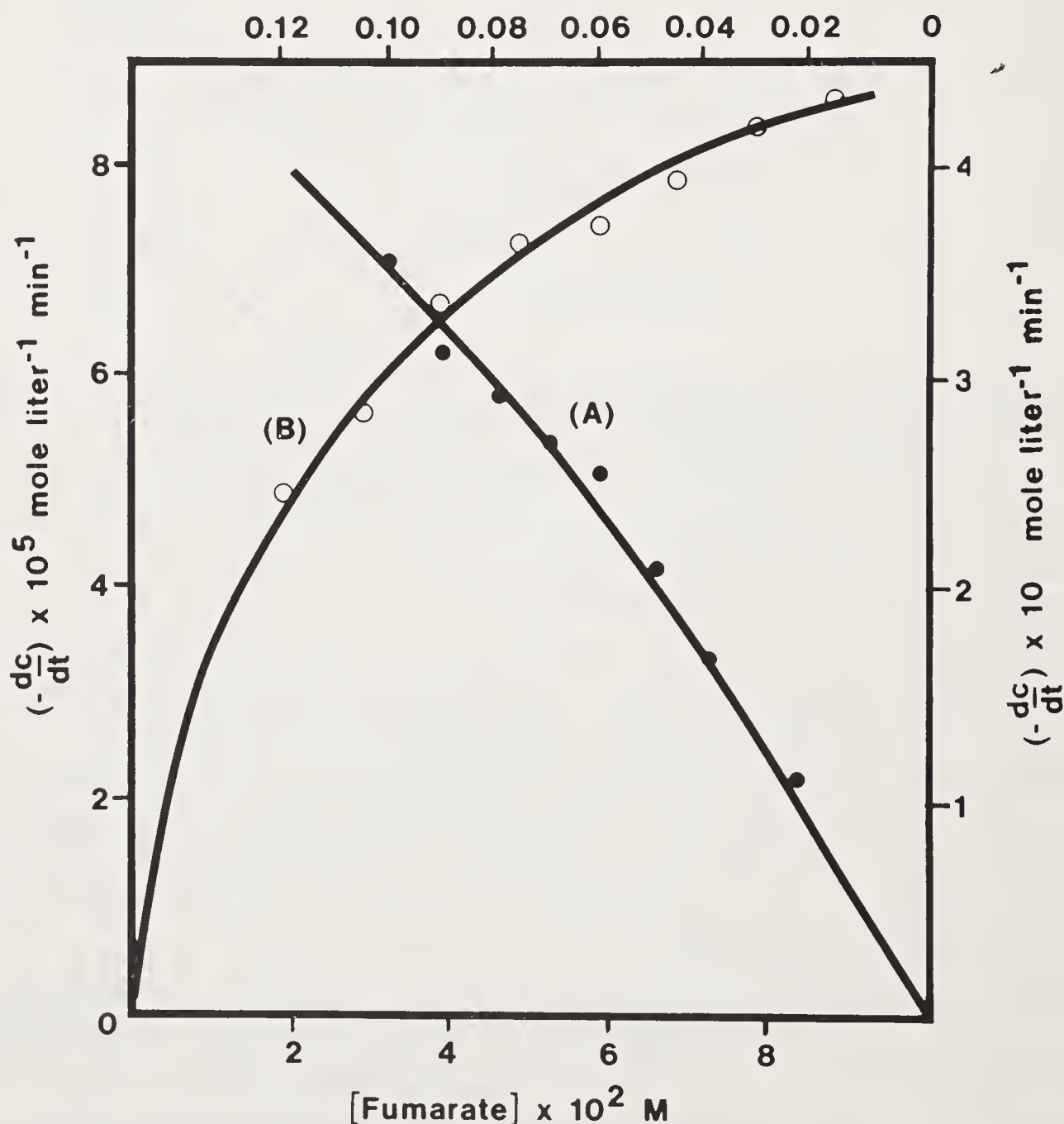


Fig. 3-5. Plots of  $-dc/dt$  vs [substrate]. (A). Effect of varying [maleate] on reaction rate at 25°C;  $[\text{NaOH}] = 2.00 \times 10^{-2} \text{ M}$ ;  $[\text{K}_3\text{Fe}(\text{CN})_6] = 2.00 \times 10^{-3} \text{ M}$ ;  $[\text{OsO}_4] = 3.93 \times 10^{-6} \text{ M}$ ;  $\mu = 0.5 \text{ M}$ ; (B). Effect of varying [fumarate] on reaction rate at 30°C;  $[\text{NaOH}] = 2.00 \times 10^{-1} \text{ M}$ ;  $[\text{K}_3\text{Fe}(\text{CN})_4] = 4.00 \times 10^{-3} \text{ M}$ ;  $[\text{OsO}_4] = 0.79 \times 10^{-6} \text{ M}$ ;  $\mu = 0.5 \text{ M}$ . From Reference 118.



*dl*-tartaric acid from fumaric acid. The rate-controlling step in these reactions is the complex formation between  $\text{OsO}_4$  and the olefin moiety of the maleic derivative. Small differences in reactivities are attributed to steric hindrance, such that fumaric acid reacts faster than maleic acid.

Singh *et al.*<sup>(118)</sup> studied the reaction of maleate and fumarate ions using the  $\text{OsO}_4$ /ferricyanide system. Interestingly, they find maleate to be more reactive than fumarate, an observation different from those of other authors studying  $\text{OsO}_4$ -catalyzed oxidation. The mechanism was examined in detail. The nearly first-order kinetics at low concentrations of fumarate tended to decrease at higher substrate concentration as shown in Fig. 3.5. The complexity of the system is more evident in Fig. 3-6. Here, the  $[\text{OH}^-]$  concentration dependence is quite different for both substrates.

Thus, they proposed that the maleic system was showing expected behavior in that the rate was first order each in  $\text{OsO}_4$  and the organic substrate

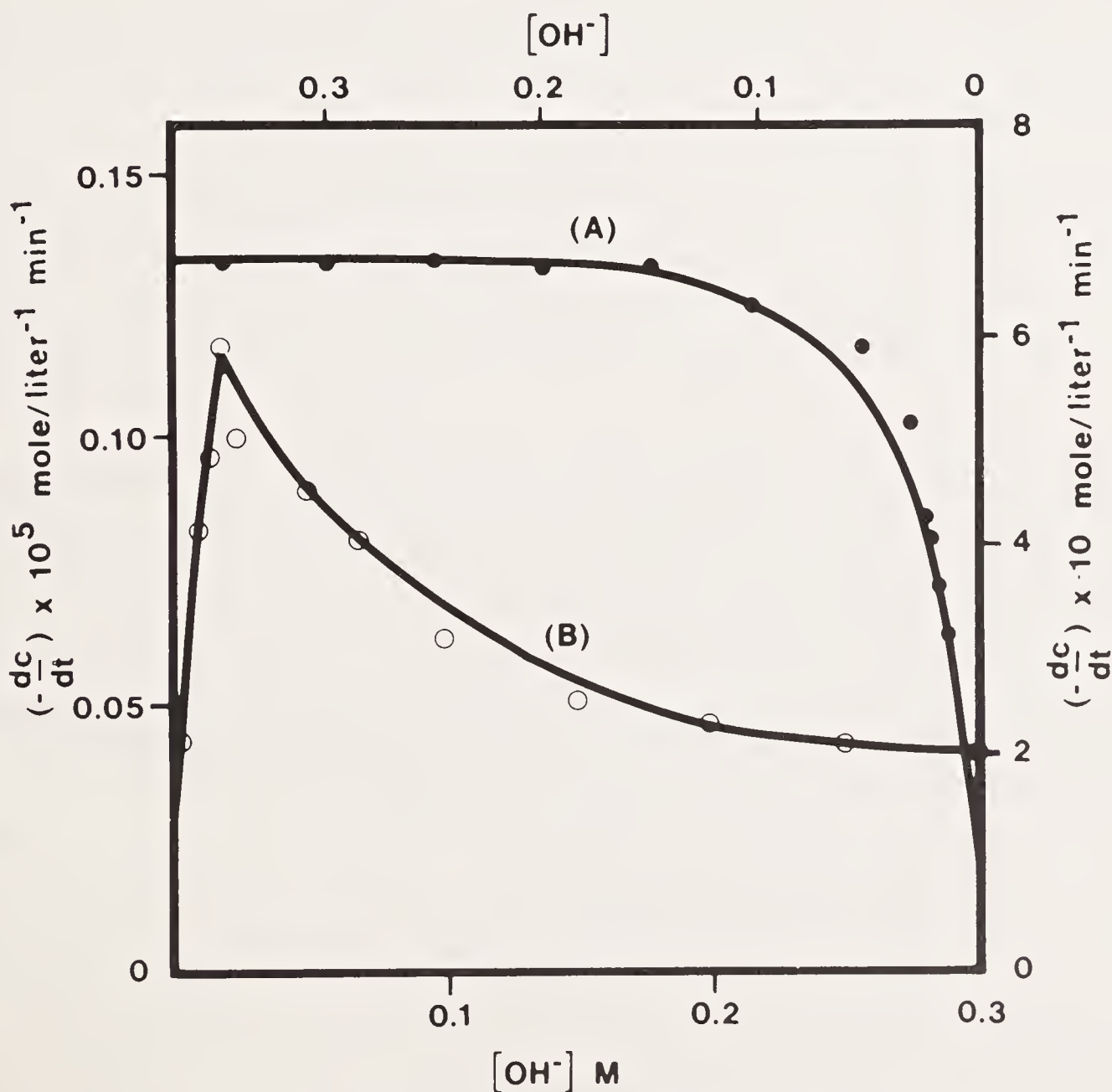
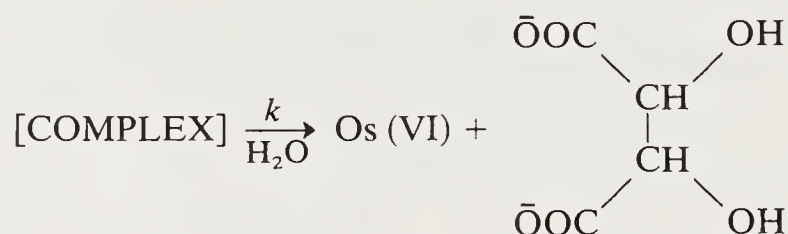
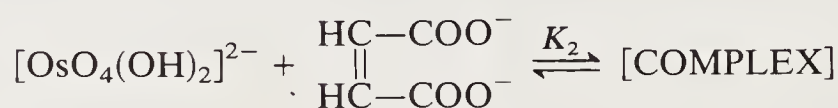
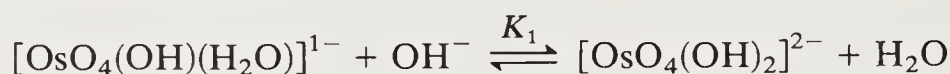
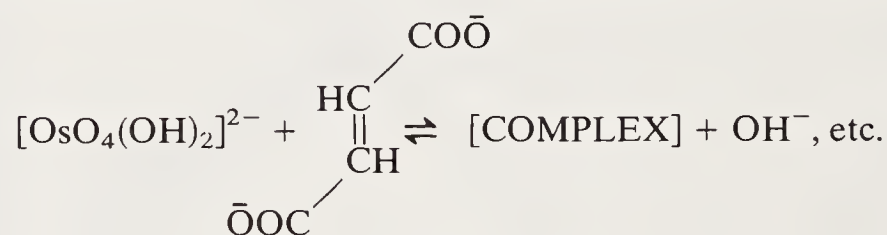
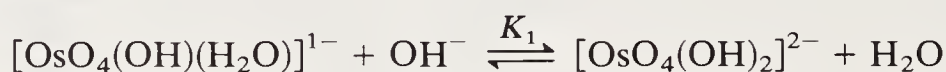


Fig. 3-6. Plots showing the effect of varying  $[\text{OH}^-]$  on the reaction rate at 25°C (A).  $[\text{maleate}] = 2.00 \times 10^{-2} \text{ M}$ ;  $[\text{K}_3\text{Fe}(\text{CN})_4] = 2.0 \times 10^{-3} \text{ M}$ ;  $[\text{OsO}_4] = 1.97 \times 10^{-6} \text{ M}$ ;  $\mu = 0.5 \text{ M}$ ; (B).  $[\text{fumarate}] = 2.00 \times 10^{-2} \text{ M}$ ;  $[\text{K}_3\text{Fe}(\text{CN})_6] = 2.00 \times 10^{-3} \text{ M}$ ;  $[\text{OsO}_4] = 3.75 \times 10^{-1} \text{ M}$ ;  $\mu = 0.5 \text{ M}$ . From Reference 118.

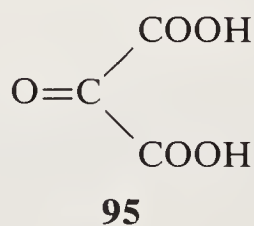
but zero order in ferricyanide. The first-order dependence on  $[\text{OH}^-]$  at low hydroxide-ion concentrations approaches zero order at higher  $[\text{OH}^-]$  concentration. To account for these observations, the following scheme was proposed.



Fumarate ion, which showed an unexpected dependence on  $[\text{OH}^-]$  concentration, was proposed to involve  $[\text{OH}^-]$  in the mechanism—as shown in the scheme below:



It should be pointed out that Singh *et al.*<sup>(118)</sup> mention a significant amount of uncatalyzed oxidation of fumarate ion by ferricyanide. The mechanistic implications are not clear. From both maleic and fumaric acid, mesoxalic acid **95** was obtained as the product. The rate differences in both isomers were proposed to be due to steric effects; however, no reason for mechanistic differences was given. These differences between oxidation reagents in terms of final products and mechanism in terms of substrates appears to be of fascinating synthetic as well as mechanistic potential.



In a still more recent study, Panigrahi and Misro<sup>(119)</sup> have examined the  $\text{OsO}_4/\text{IO}_4^-$  system with maleate and fumarate ions. Here, although they observe the fumaric activity to be greater than the maleic reactivity as did Zelikoff,<sup>(117)</sup> they also observe a first-order dependence on  $[\text{OH}^-]$  concentra-

tion in both cases. Like Zelikoff,<sup>(117)</sup> they observed a high entropy of activation.

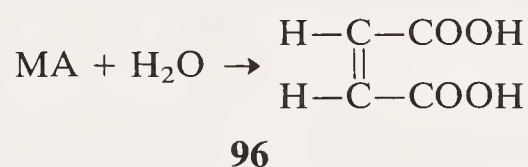
Tartaric acid **93**, which is the main product in most of the processes discussed, has found use as a food and beverage acidulant.<sup>(260)</sup> Its complexing ability is used for metal cleaning and finishing.<sup>(261)</sup>

Epoxysuccinic acid **92** has not found a major outlet but its functionality shows significant potential.

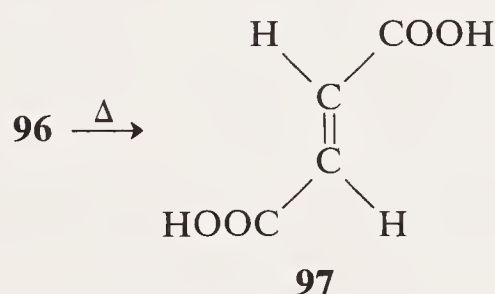
### 3.4. REACTIONS OF ANHYDRIDE FUNCTION

#### 3.4.1. Hydrolysis

Maleic anhydride, like most other anhydrides, can be hydrolyzed to the corresponding acid **96**. Simple dissolution of maleic anhydride in water suffices



for the purpose. The reaction, as expected, is exothermic. This easy hydrolysis of maleic anhydride is used in the recovery of maleic acid during production (see Chapter 2). Controlled hydrolysis produces the *cis* (Z) acid, i.e., both the carboxyl groups of the acid are on the same side of the double bond. By prolonged warming, the maleic acid can be converted to fumaric acid which is *trans* (E) acid **97**.



This phenomenon is common among all the ring-opened products from the anhydride. The other ways to bring about such isomerization are discussed elsewhere along with applications (see Chapter 1).

Hydrolysis rates of other cyclic anhydrides and maleic anhydride have been compared. Rivett and Sidgewick examined the kinetics of hydrolysis by the conductometric method.<sup>(120)</sup> Their results are summarized in Table 3.6.

The examination of relative rates of hydrolysis show maleic to be the most reactive. No  $\text{H}^+$  ion catalysis was observed. Eberson and Landstrom have examined the rate of hydrolysis of a number of cyclic anhydrides.<sup>(121)</sup> In their study, they chose a number of anhydrides with different kinds of strains, namely, conformational, angle, and torsional. Maleic anhydride was found to react 10 times faster than succinic. Eberson and Landstrom<sup>(121)</sup> and

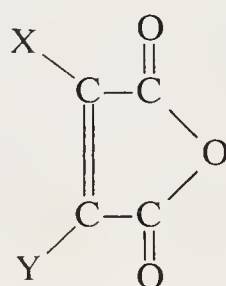


Table 3.6. Relative Rates of Hydrolysis and Relative Dissociation Constants of Some Anhydrides<sup>a</sup>

Anhydride	Relative rate	Relative Dissociation Constant
Acetic	0.99	—
Succinic	1.00	1.00
Methylsuccinic	1.39	1.30
Itaconic	1.12	1.82
Maleic	9.96	182.0
Phthalic	3.99	18.3
Citraconic	6.62	51.5

<sup>a</sup> From Reference 120.

Rivett and Sidgewick<sup>(120)</sup> have assigned this to the strain in the MA ring. In the series of anhydrides studied by Eberson and Landstrom,<sup>(121)</sup> only in those anhydrides which had the following structure, where  $x$  and  $y$  was part of a ring (alicyclic), were reactivities comparable to MA found; i.e., the anhydride was a derivative of maleic anhydride itself.



Without becoming further involved in the ease of the ring opening, an important aspect of the strength of maleic acid and fumaric acid should be

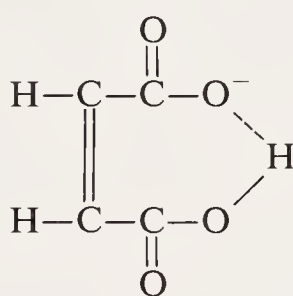
Table 3.7. Dissociation Constants and pK Values of Some Acids<sup>a</sup>

Acid	Step	$K$	pK
Acetic		$1.76 \times 10^{-5}$	4.75
Maleic	1	$1.42 \times 10^{-2}$	1.83
	2	$8.57 \times 10^{-7}$	6.07
Fumaric	1	$9.30 \times 10^{-4}$	3.03
	2	$3.62 \times 10^{-5}$	4.44
Phthalic	1	$1.30 \times 10^{-3}$	2.89
	2	$3.90 \times 10^{-6}$	5.51
Malic	1	$3.90 \times 10^{-4}$	3.40
	2	$7.80 \times 10^{-6}$	5.11

<sup>a</sup> Reprinted in part with permission from *Handbook of Chemistry and Physics*, R. C. West, ed., Chemical Rubber Company, Cleveland, Ohio (1979). Copyright © 1970, The Chemical Rubber Company.

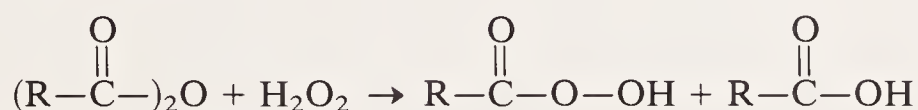
considered. In Table 3.7, the dissociation constants and  $pK$  values of some organic acids are given for comparison.

It can be seen that maleic and fumaric acids are stronger than acetic and succinic acids. Also interesting is the fact that the second dissociation constant for maleic acid is much lower than that for succinic acid. Part of this difference between the first and second dissociation constants is ascribed to the proximity of carboxyl groups in the *cis* configuration and the resultant electrostatic effects.<sup>(122–125)</sup> This increases the energy necessary for formation of the second anion. Such a difference is also seen in phthalic acid, although to a slightly lesser degree. The electrostatic effect, however, is not the only explanation. McCoy<sup>(124)</sup> has studied  $pK$  values of *cis*-dicarboxylic acid and suggests that hydrogen bonding may play a significant role.

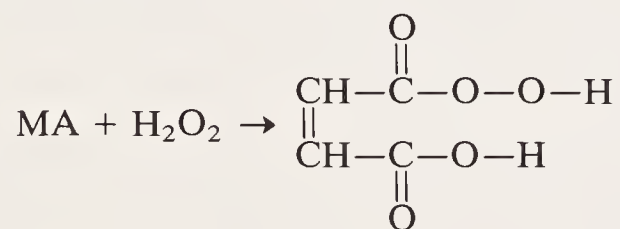


### 3.4.2. Permaleic Acid

The formation of a peracid by the reaction of an acid anhydride with hydrogen peroxide is well known.<sup>(126)</sup>



Cyclic dicarboxylic anhydrides also undergo this reaction. However, it was not until 1962 that White and Emmons<sup>(127,128)</sup> first showed the formation of permaleic acid **98**. Generally, the reaction is carried out by reacting MA with a concentrated hydrogen peroxide solution in methylene chloride. The reaction is carried out at ice temperature. Other inert solvents such as chloroform, DMF, formamide, formic acid, benzene, and dioxane, have been used.

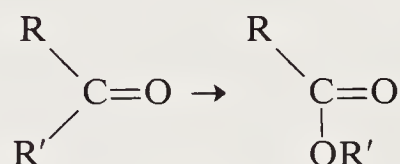


**98**

White and Emmons<sup>(127)</sup> in an excellent report claim that although permaleic acid is not quite as potent a peracid as trifluoroperacetic acid, it is stronger than other laboratory acids. It is reasonably stable in methylene chloride and decomposes ~5% in 6 h at ambient temperature. One additional

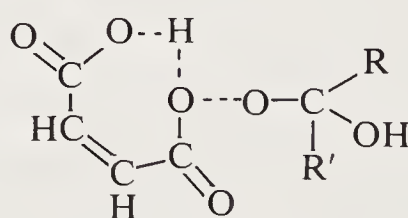
advantage of permaleic acid is that as the reaction proceeds, maleic acid is formed, which, being insoluble in the medium, precipitates out. This facilitates work-up, since filtration is all that is required to remove maleic acid.

Permaleic acid is an excellent reagent for the Baeyer–Villiger reaction.<sup>(127,129)</sup> In the latter, an acyclic or a cyclic ketone is oxidized to the corresponding ester.

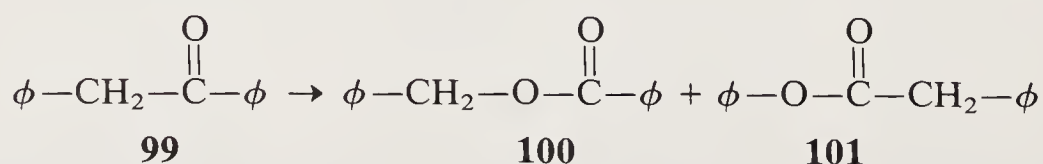


In Table 3.8, a number of ketones and yields of the product esters from these are given using permaleic acid as the reagent. The yields reported in Ref. 129 are also listed for comparison.

The greater activity of permaleic acid compared to other peracids such as peracetic, performic, or perphthalic have been attributed, by White and Emmons, to lower basicity and higher stability of the maleic acid monoanion (see Sect. 3.4.1). It is reasoned that the low basicity–high stability combinations allow the transfer of electron-deficient oxygen in the transition state with lower energy expenditure. In addition, a more favorable entropy of activation for permaleic acid is provided for in the transition state. It is known from other studies that the rate-determining step is the acid-catalyzed decomposition of the peracid–ketone complex. White and Emmons<sup>(127)</sup> argue, based on a study of molecular models, that acidic hydrogen on the carboxyl group in permaleic acid is in closer proximity to the oxygen where the negative charge is developing in the transition state. This favorable entropy provides for autocatalysis in permaleic acid reactions.



In Table 3.8, it is interesting to note that oxidation of desoxybenzoin **99** with permaleic acid gives benzyl benzoate **100** as the predominant product. On the other hand, trifluoro-peracetic acid gives a 1 : 1 mixture of **100** and **101**.<sup>(131)</sup>



Hawkins<sup>(130)</sup> has used permaleic acid for the Baeyer–Villiger oxidation of cyclohexanone to obtain cyclohexanolide in a 90–100% yield. He has shown that if any free hydrogen peroxide is present, the yield could suffer

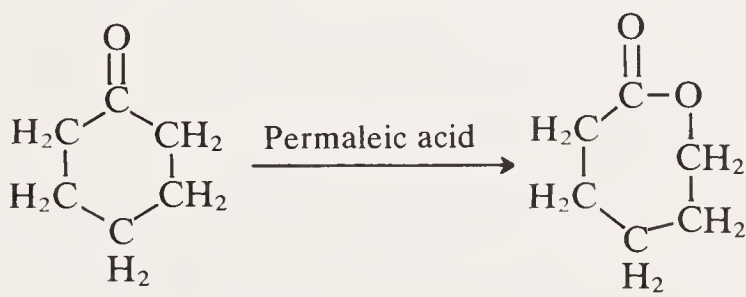


Table 3.8. Oxidation of Ketones to Esters With Permaleic Acid<sup>a</sup>

Substrate	Time of reaction (h)	Product	Boiling point, °C	Yield %	Yield % <sup>b</sup>
Methyl isobutyl ketone	3	Isobutyl acetate	115–116°	72	—
Diisobutyl ketone	3	Isobutyl isovalerate	52–54° (10 mm)	83	—
Octanone-2	3	Hexyl acetate	56–58° (10 mm)	71	51
Cyclooctanone	3	$\omega$ -Hydroxyoctanoic acid lactone	73–74° (9 mm)	67	—
Estrone acetate	12	Estronolactone acetate	m.p. 141–144°	40	57–63
Benzophenone	2	Phenyl benzoate	m.p. 68–70°	70	quantitative
Acetophenone	2	Phenyl acetate	89–90° (17 mm)	70	33, 63
Desoxybenzoin	2	Benzyl benzoate Phenyl phenylacetate		75	—

<sup>a</sup> From Reference 127.  
<sup>b</sup> From Reference 129.

due to cyclohexanone peroxide formation. The conditions to achieve hydrogen-peroxide-free permaleic acid have been described by Hawkins.<sup>(130)</sup>



In addition to the Baeyer–Villiger oxidation of ketones, permaleic acid can also be an excellent reagent for oxidizing primary amino compounds to their nitro derivatives (Table 3.9).<sup>(127)</sup> Epoxidation of olefins can also be

Table 3.9. Oxidation of Aromatic Amines With Permaleic Acid<sup>a</sup>

Substrate	Product	Melting point	Yield (%)
<i>p</i> -Nitroaniline	<i>p</i> -Dinitrobenzene	171–173°C	87
2,4,6-Tri-bromoaniline	2,4,6-Tribromonitrobenzene	122–124°C	90
2-Naphthylamine	2-Nitronaphthalene	77–79°C	40

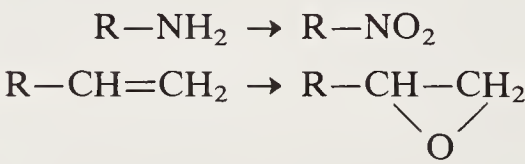
<sup>a</sup> From Reference 127.

Table 3.10. Epoxidation of Olefins With Permaleic Acid<sup>a</sup>

Substrate	Product	Boiling point	Yield (%)
Octene-1	Octene-1 oxide	51–54°C (10 mm)	80
Methyl methacrylate	Methyl α-methylglycidate	50°C (16 mm)	74
Ethyl acrylate	Ethyl glycidate	60–62°C (17 mm)	33
Diallyl sulfoxide	Diallyl sulfone	88–90°C (0.4 mm)	87

<sup>a</sup> From Reference 127.

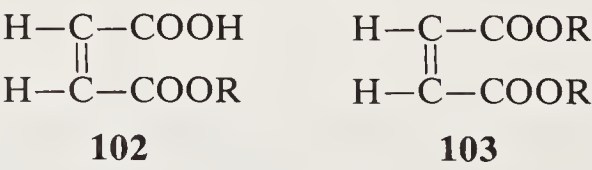
achieved using this reaction. Yields, as can be seen in Table 3.10, are generally high for the epoxidation reactions.<sup>(127)</sup>



As can be seen from the foregoing, permaleic acid is an excellent reagent where a peracid is called for. Especially in the Baeyer–Villiger oxidation, it may be the reagent of choice. Recovered maleic acid can be recycled easily and, as mentioned earlier, the recovery is facilitated by the insolubility of the acid in the reaction medium.

3.4.3. Esterification

MA, being an internal anhydride, can give rise to two different ester derivatives upon reaction with an alcohol. As will be seen below, both can be formed readily and both have found significant use commercially.



Siegal and Moran<sup>(132)</sup> observed that MA and phthalic anhydride titrated only half the expected titer when the anhydrides were dissolved in cold ethanol. In a study that followed, they observed that MA reacted almost instantaneously with a number of primary alcohols as shown in Table 3.11. It is interesting to note that the only secondary alcohol tried, i.e., isopropyl alcohol, did not react at all. Incomplete esterification of *n*-propyl alcohol was also not explained. The kinetics and activation parameters for monoalkyl maleate formation have been determined recently.<sup>(278,294)</sup> In any case, it appears safe to say that the reaction between maleic anhydride and lower primary alcohols is nearly complete at room temperature. Monoester formation is a key reaction involving maleic anhydride and a number of its polymeric derivatives. This

Table 3.11. Monoester **102** Formation From Alcohols and MA<sup>a</sup>

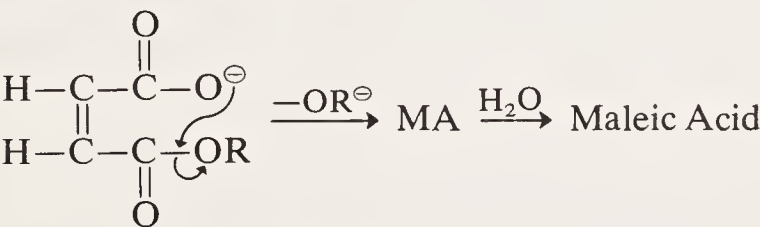
Alcohol	Moles Alcohol : anhydride	Percentage of original theoretical titer						
		1 min	10 min	½ h	1 h	1½ h	3 h	4½ h
Methyl	Large excess of alcohol	50.0						
Methyl	2 : 1	49.9	49.6	49.9				51.0
Ethyl	2 : 1	50.7	50.9	51.4				
Propyl	2 : 1	45.8	45.0	46.4			46.0	
<i>i</i> -Propyl	2 : 1	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Butyl	2 : 1	49.0	...	48.8				
Butyl	4 : 1	52.7	52.7	50.6				
Amyl	2 : 1	52.8	52.9	52.5	51.5			
Ethylene glycol	2 : 1	48.8	...	50.4				

<sup>a</sup> Reprinted with permission from *J. Am. Chem. Soc.* **69**, 1457 (1947). Copyright © 1947, American Chemical Society.

is an efficient reaction, since in many cases, attainment of homogeneity may give quantitative yield.<sup>(133)</sup>

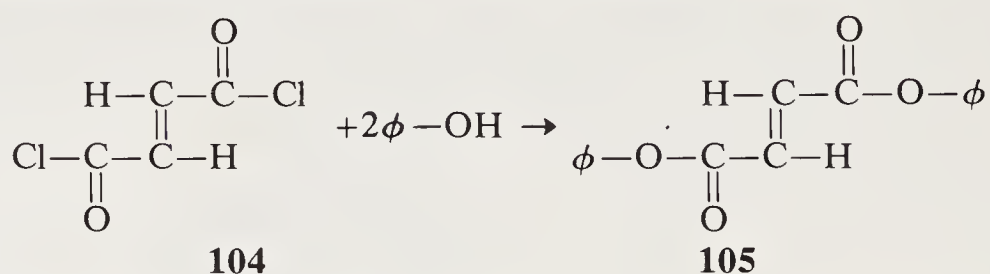
Holsopple<sup>(138)</sup> has examined half-ester formation with long-chain alcohols such as dodecyl, tridecyl, and heptadecyl alcohols. Here, the reaction is not as rapid as expected. An optimum temperature for each conversion has been reported.

It may be interesting to digress and examine the solvolysis of maleate half-esters. Bruice and Pandit<sup>(134)</sup> have examined the hydrolysis of substituted phenyl esters of a number of anhydrides. Anchimeric assistance by the carboxyl group is invoked in the hydrolysis giving rise to the anhydride. They suggest that the solvolysis of the resulting anhydride is the slow step in the conversion of monoalkyl maleate to maleic acid.

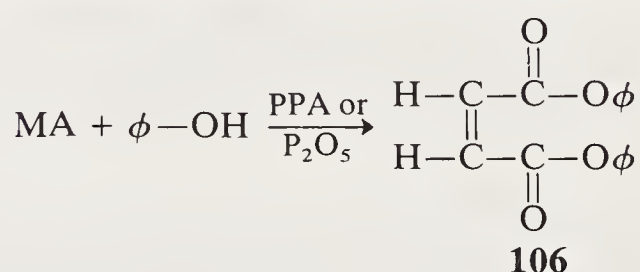




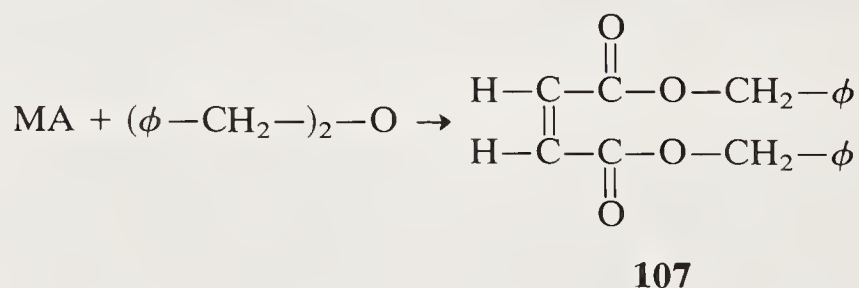
an azeotropic agent. Among the common catalysts tried are sulfuric acid<sup>(135,136)</sup> and sulfonic acid ion-exchange resins. Fumaric acid esters are made in the presence of sulfuric acid from the acid. Fumaroyl chloride **104** is utilized to



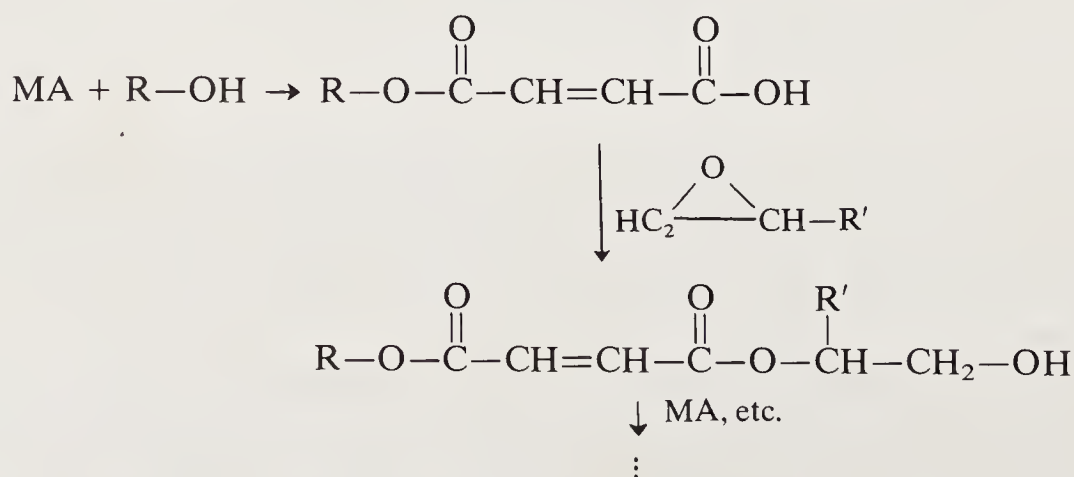
make aryl fumarates **105** from phenols.<sup>(137)</sup> Diaryl maleates **106** can be prepared by the reaction of MA and phenol. Dehydration in this case is effected by phosphorus pentoxide<sup>(139)</sup> or polyphosphoric acid (PPA).<sup>(140)</sup> Regenerable dehydrating agents such as silica may hold potential.



Dibenzyl esters **107** have reportedly been formed from the acid-catalyzed reaction of dibenzylether with MA.<sup>(142)</sup> However, the product is obtained in low yields.



During polyester formation the reaction takes advantage of the ready monoester formation from MA with alcohols and easy esterification of acids with epoxides<sup>(141)</sup> to yield hydroxy esters. The newly formed hydroxy ester provides the alcohol to continue the chain, as illustrated below. (See Chapter 12.)



Dharwadkar and Hussain<sup>(133)</sup> have recently studied the kinetics of dibutyl maleate formation from *n*-butanol and MA. The esterification was carried

out using varying catalyst levels at 85–115°C. This examination was done for the purpose of reactor design. Some of their kinetic conclusions are interesting. As expected, the reaction is accelerated by increasing temperature. The initial rate of the reaction increases with increasing catalyst concentration as well.

The intriguing aspect of Dharwadkar and Hussain's study is the fact that they observed a second-order rate dependence on the concentration of the half-ester. Since the reaction is an esterification process, it would have been expected to give a first-order dependence on both the reactants. No explanation was forwarded by these authors for the discrepancy. Merca *et al.*<sup>(294)</sup> have recently reported the kinetics of diethyl maleate formation from the half-ester and ethanol to be second order overall. Activation parameters are also given.

As mentioned earlier, mono and dialkyl esters are commercially important in a number of applications.<sup>(144,145)</sup> The single largest commercial use of MA is for the manufacture of unsaturated polyesters. The latter are used in automobile and marine applications.<sup>(146)</sup> Besides, they have been extensively employed as intermediates for wetting agents, surfactants, dye leveling agents, and cosmetic ingredients (see Sec. 3.2.6). Dialkyl esters have been widely used as monomers and as plasticizers<sup>(144)</sup> (see chapters 8–10). Dialkyl maleates have often been used as reactants or monomers in place of MA since the esters are liquids and hence easier to handle. Esters of MA are also employed as intermediates for insecticides and as insecticides themselves.<sup>(143)</sup>

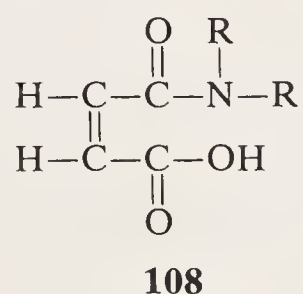
The mono and dialkyl esters have been claimed as tobacco flavoring agents.<sup>(142)</sup> A variety of fruit flavors are obtained at low concentrations (0.001–1.0%) of the esters.

Monoesters made from MA and polyhydroxy alcohols, e.g., pentaerythritol, sorbitol, dipentaerythritol, and tripentaerythritol, have been claimed to be useful as detergent builders.<sup>(136)</sup>

### 3.4.4. Reactions with Amines

#### 3.4.4.1. Maleamic Acids

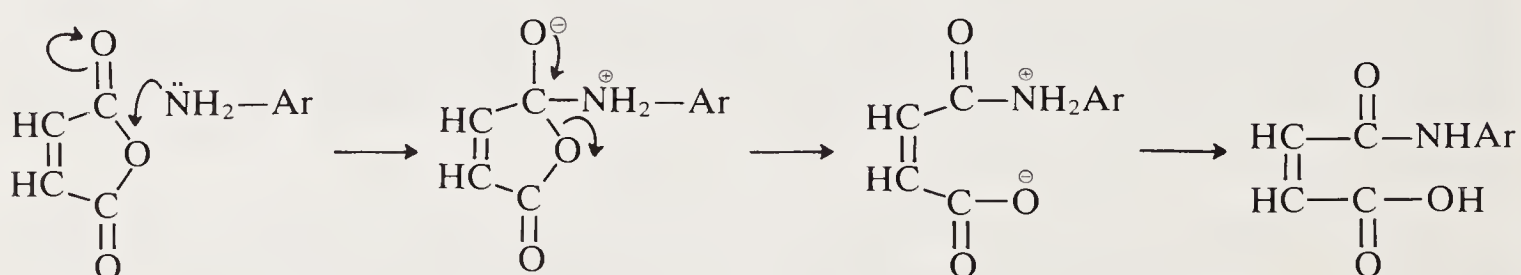
When MA reacts with ammonia, a primary or a secondary amine, acylation occurs resulting in formation of an amide derivative. This half-amide derivative is called maleamic acid **108**. When one of the R groups in **108** is aryl, often the product is referred to as a maleanilic acid.



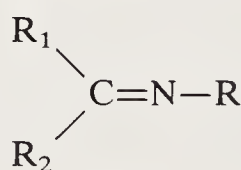
Anhydrous ammonia reacts with MA in benzene solution under ambient conditions. The ammonium salt initially formed is dissolved in water and heated until loss of ammonia odor and then acidified to obtain a 70% yield of the maleamic acid **108** ( $R = R' = H$ ).<sup>(147)</sup> Takaya and coworkers<sup>(148)</sup> have shown that a 95% yield of the product can be obtained by conducting the reaction at 50°C for 5 h.

Primary amines also give good to excellent yields of the *N*-alkylmaleamic acids.<sup>(149,158)</sup> Similarly, aromatic amines also give high yields of the maleanilic acids.<sup>(151-153)</sup> For example, maleanilic acid itself **108** ( $R = \phi$ ,  $R' = H$ ) is obtained in 97-98% yield.<sup>(153,154)</sup> The reaction is also applicable to heterocyclic primary and secondary amines.<sup>(155-157,159)</sup> It may be added that since maleic derivatives are known to add amines across the double bond and are also known to isomerize to the fumaric derivatives, contributions of these side reactions often give lower yields.

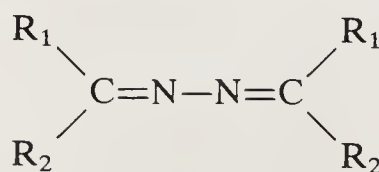
Kretov and Kulchitskays<sup>(152)</sup> have studied the rate of maleanilic acid formation as a function of substitution on the aromatic ring. They observed that the rate of the reaction increased with increasing basicity of the amine reagent. These results are in agreement with the following scheme.



In the past, reactions of Schiff's bases **109** (made from primary amines and carbonyl compounds) with MA have been reported to yield maleamic acids.<sup>(165-168)</sup> However, a mole of water is needed to explain the products. It

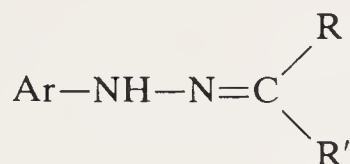
**109**

may be assumed, therefore, that impure MA or inadvertent inclusion of water occurred in those reactions. Tamayo and Alvarez<sup>(169)</sup> have demonstrated that no reaction occurs between a Schiff's base and MA at 160°C if the complete absence of moisture is assured. Azines **110** give a 2:1 MA:azine adduct resulting from a 1,3-cycloaddition process. (See Chapter 7.)

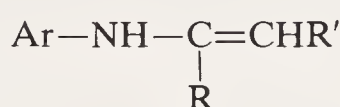
**110**



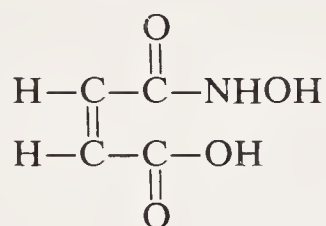
Arylhydrazones<sup>(170)</sup> **111** and enamines<sup>(171)</sup> **112** also reportedly yield maleamic acid derivatives on reaction with MA. In some cases, the initial

**111**

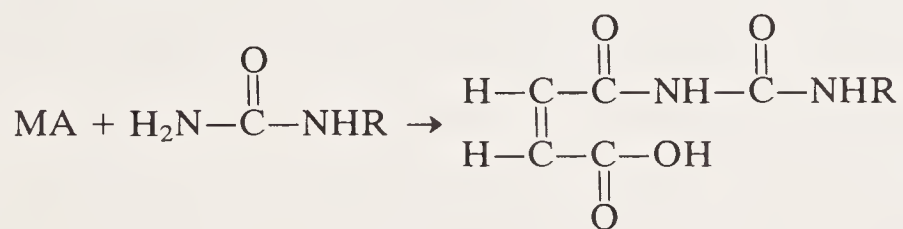
maleamic acid product may further react to yield heterocyclic compounds as shown by Szilagyi and Wamhoff.<sup>(279)</sup> An internal Michael addition was considered responsible for the cyclization (see Sec. 3.2.11).

**112**

The hydroxamic acid derivative shown below is formed on reacting MA with hydroxylamine.<sup>(160,198)</sup> The *cis* isomer is a bactericidal and fungicidal agent.<sup>(161)</sup> Alkylhydroxylamines (NH<sub>2</sub>OR) also react similarly.<sup>(164)</sup>



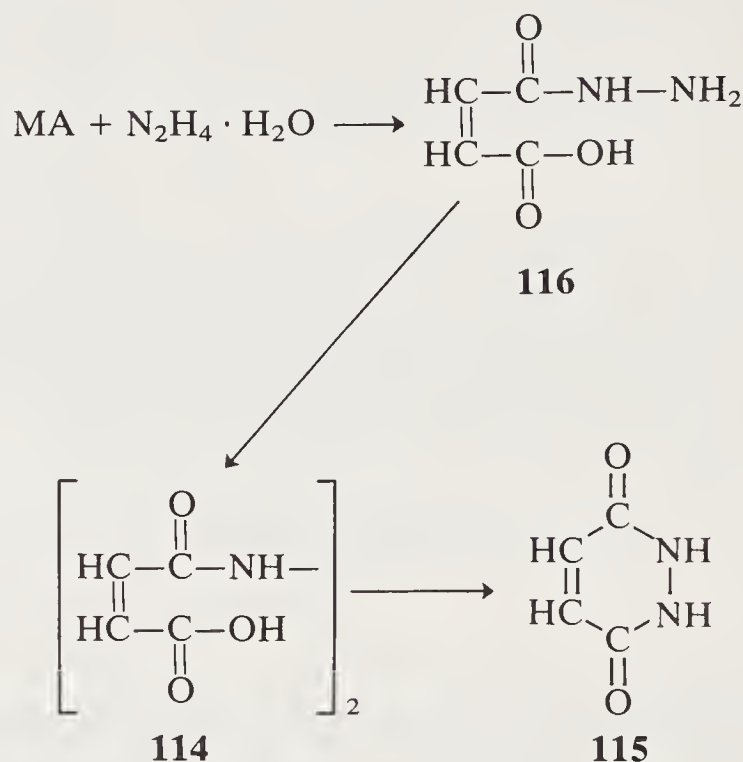
Ureas have been acylated with MA to obtain maleuric acids **113**.<sup>(150,162,163)</sup> Dunlap and Phelps<sup>(150)</sup> reported the reaction of urea and MA but no yield was given. However, Tawney and coworkers<sup>(163)</sup> report 50% yield **113** (R = H). Higher yields (up to 95%) could be obtained on recycling of the mother liquor. Substituted ureas gave modest yields.

**113**

R = H, 50–95%; R = Ph, 32%; R = *n*-Bu, 58%; R = *t*-Bu, 85%

Reaction of MA with hydrazine is of considerable importance, commercially as well as synthetically. For example, hydrazine hydrate forms two different products with MA depending on the conditions of the reaction. Thus, when 2 moles of hydrazine hydrate are added to a solution of 2 moles of MA in acetic acid, 1,2-dimaleic acid hydrazide **114** is formed in a 96% yield.<sup>(172)</sup> However, on heating an acetic acid solution of the two in equimolar quantities,

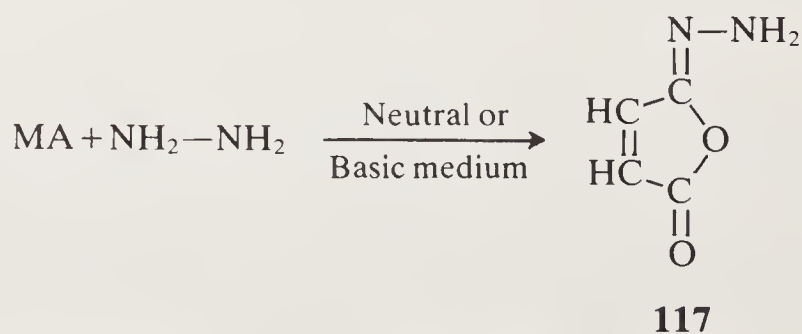
an 83% yield of maleic hydrazide **115** is obtained. At higher temperature **114** can be converted to **115** as shown in the scheme below.



It was observed that **114** could be converted to **115** by refluxing in water, but remained unchanged in polyphosphoric acid. Therefore, it was suggested that **116** was an intermediate for both processes, and that hydrolysis of **114** to **116** was necessary for the formation of **115**.

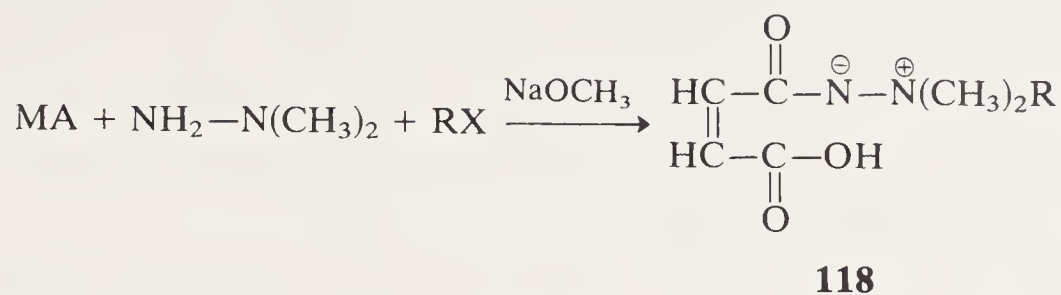
Formation of maleic hydrazide was first reported by Curtius and Feusterling<sup>(173)</sup> but Feuer *et al.*<sup>(172)</sup> believed that Curtius obtained a mixture of products. A number of authors have reported the preparation of **115** by the reaction of the hydrazinium salt of a mineral acid and MA.<sup>(174-176)</sup> This product is a popular herbicide and a plant growth regulator.

Dunkels and Hillers<sup>(177)</sup> have shown that the nature of the product formed from hydrazine and MA depends also on the acidity of the medium. Thus, under neutral or basic conditions, **117** is formed whereas acidic medium gives rise to **115**. Fumaryl dihydrazide is made in low yields by the reaction of fumarate ester and hydrazine.<sup>(173-178)</sup>



Reaction of MA with mixtures *N,N*-dimethylhydrazine and alkyl halide in the presence of a base gives rise to an aminimide derivative **118**.<sup>(276,277)</sup> Preformation of the hydrazinium salt by reaction of *N,N*-dimethylhydrazine

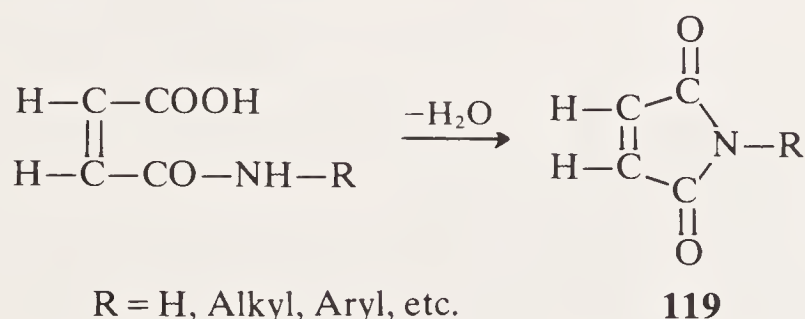
with the alkyl halide is beneficial. A number of alkyl and aralkyl halides can be employed.<sup>(276)</sup>



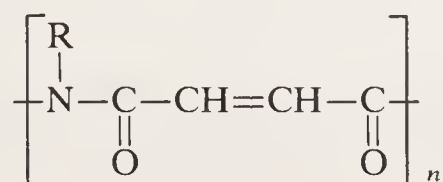
Arylhydrazines on reaction with MA can give rise to the corresponding maleamic acid.<sup>(179,180)</sup> These products can be cyclized to give the pyridazine ring.<sup>(181)</sup> *N,N*-disubstituted hydrazines give high yields of the amic acid derivatives.<sup>(182)</sup>

#### 3.4.4.2. Maleimides

Maleamic acids, produced on reaction of MA with ammonia and primary amines, on cyclization can yield maleimides **119**.



A number of ways have been used to achieve the cyclization since maleimides are important monomers. Simple heating of maleamic acid with slow removal of a mole of water generally provides for low yields of the imides as reported by Rinkes.<sup>(183)</sup> An acid catalyst was used to help the cyclization and the reaction is somewhat facilitated by an azeotropic removal of water. Coleman *et al.*<sup>(149)</sup> studied cyclization of *N*-alkylmaleamic acids **119** using xylenes to remove water at 180°C. Even here, the yields were 15–25%. Coleman and coworkers suggested that by removal of the solvent under reduced pressure, the yield could be improved to 50% (R = *n*-Bu), with a resin formed as a by-product. The formation of the resin could not be prevented using inhibitors for radical polymerization such as hydroquinone and *p*-*t*-butylcatechol. By spectral analysis, Coleman *et al.*<sup>(149)</sup> deduced that the polymer could be a linear condensation product of maleamic acid.

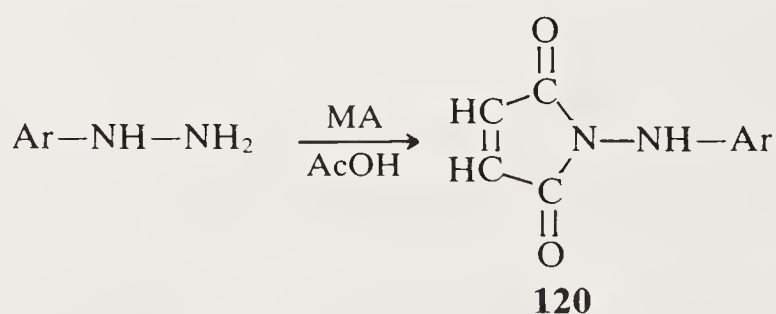




Although no geometries have been indicated in most of these synthetic works, it is known that amines isomerize maleic acid derivatives to the thermodynamically more stable fumaric acid derivatives. Furthermore, cyclization to imides is much more easily obtained with succinic acid and phthalic acid.<sup>(155)</sup> It may be concluded, therefore, that low yields of cyclization in maleamic acid is not so much due to lack of reactivity as to the formation of less reactive fumaramic derivative by isomerization.

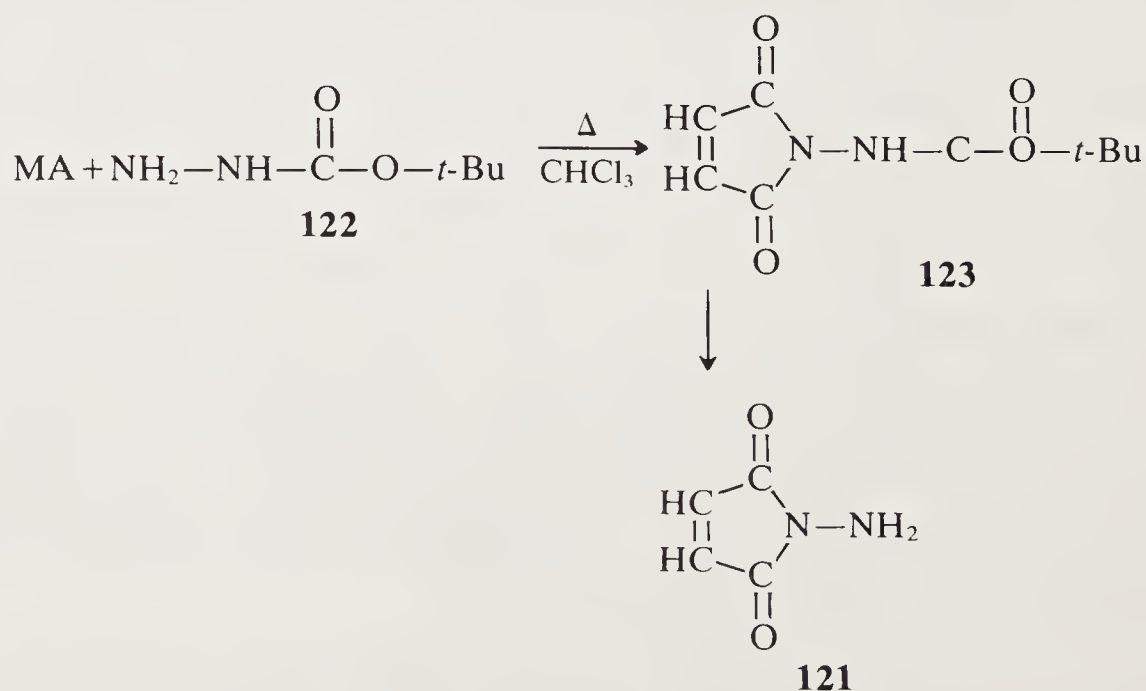
A number of other dehydrating agents have been examined. Searle's acetic anhydride/sodium acetate usually gives good yield.<sup>(153,154,281)</sup> Other reagents such as  $\text{Ac}_2\text{O}/\text{NR}_3$ , thionyl chloride, acid chlorides, chloroformates,  $\text{SbCl}_5$ ,  $\text{P}_2\text{O}_5$ , and DCC, have been utilized. (However, see more information on isomaleimide. See Refs. 164, 186, 197, 280, 282, and 283).

Jolles<sup>(179)</sup> has reported that the arylhydrazines react with MA in refluxing glacial acetic acid to form the imides **120**. Similarly maleamic acids from



*o,m,p*-chloro and bromo aniline cyclize in the presence of acetic anhydride to **119** ( $\text{R} = o,m,p$  subst-phenyl).<sup>(181)</sup>

Hydrazine, as was seen earlier, produces a pyridazine nucleus with ease. The *N*-amino derivative **121** has not been isolated from this reaction. The latter can be made by the reaction of MA with *tert*-butyl carbamate **122** followed by decomposition of the product **123** with an acid.<sup>(206)</sup>



In addition to thermal dehydration<sup>(184,185)</sup> a number of reagents have also been used to achieve this cyclization. Among these are phosphorus

Table 3.12. Yields of Substituted Maleimide<sup>a</sup>

Product <b>119</b> R=	Yield %
C <sub>6</sub> H <sub>11</sub>	91 <sup>b</sup>
Et	69
Ph	82

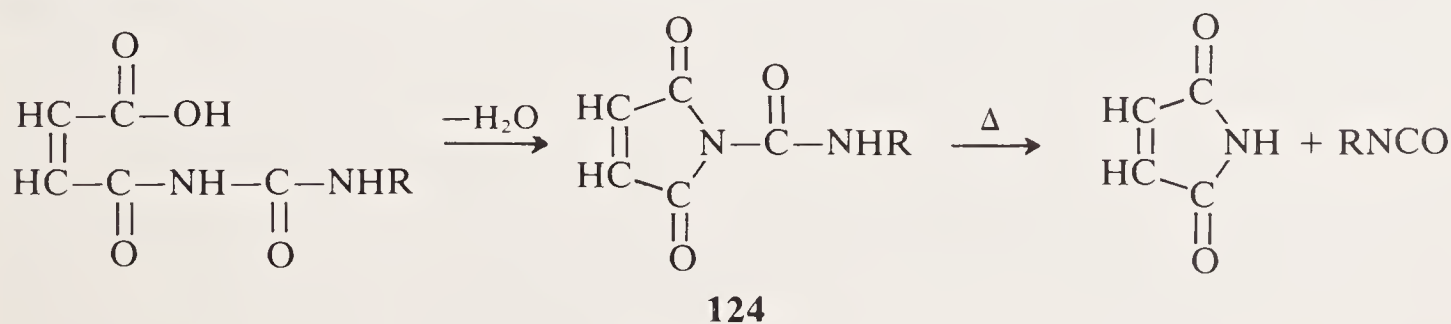
<sup>a</sup> From Reference 188.<sup>b</sup> 30–60% yield by conventional methods.

pentoxide<sup>(186,187)</sup> phosphorus trichloride,<sup>(187)</sup> and acetic anhydride.<sup>(153,186)</sup> Direct dehydration of MA and ammonia in the vapor phase over Al<sub>2</sub>O<sub>3</sub><sup>(191)</sup> and zeolites, etc., has been described. The use of acetic anhydride with sodium acetate or potassium acetate<sup>(153,154,186)</sup> reportedly gives better yields of *N*-arylmaleimide and is generally the method of choice for direct preparation.<sup>(154)</sup> Most of these methods, though successful to various degrees, require expensive reagents or a recycle of the reagent. Thus, there is no single economic process to prepare maleimide or its derivatives. This, in part, has hampered the development of imides as useful monomers.

Some effort has been put into achieving economic pathways to imides. Workers at Farbwerke Hoechst A.G. have claimed that the efficiency of thermal dehydration can be increased by the presence of an inert gas carrier, e.g., superheated steam, nitrogen, etc.<sup>(188)</sup> The reactions were carried out at 220–280°C, in the presence of a catalyst such as phosphoric acid, *p*-toluene-sulfonic acid, and potassium hydrogen sulfate. Table 3.12 summarizes the best yields obtained. Isolation of the product was reportedly simple.

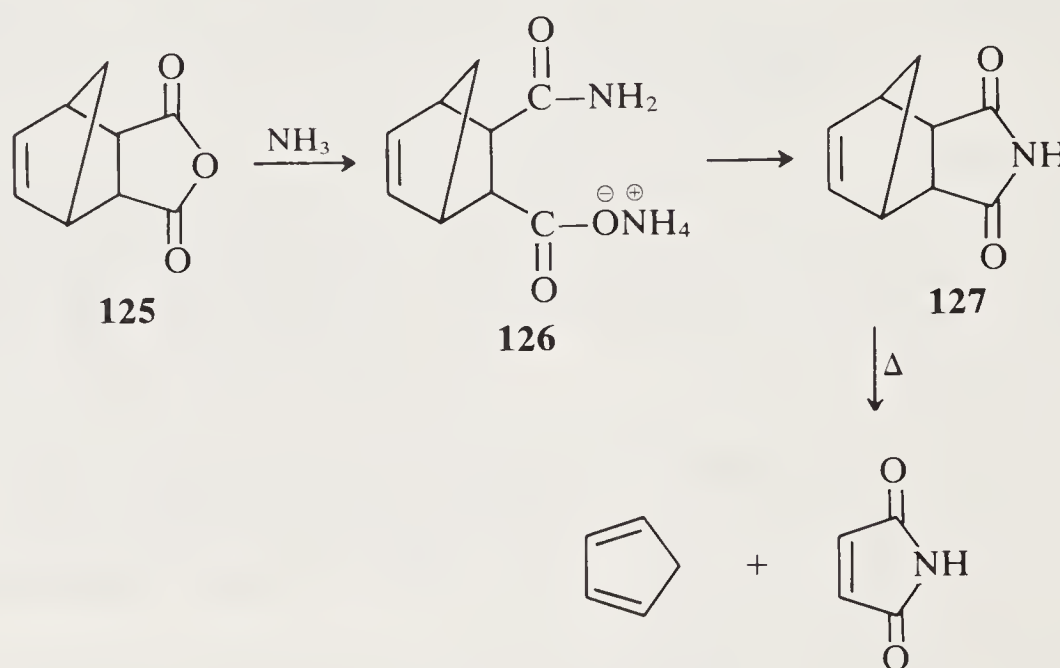
In a later patent,<sup>(189)</sup> amine salts of maleic acid were shown to be equally reactive for the purpose. MA and NH<sub>3</sub> passed over dehydrating catalysts in the vapor phase yield maleimide.<sup>(191)</sup>

Maleimides **119** can be obtained by indirect methods also. Tawney *et al.*<sup>(163)</sup> have utilized the reaction of MA with urea and alkylureas to obtain *N*-carbamylmaleimide **124**. The latter on thermolysis in DMF produces maleimide and isocyanate as a by-product.

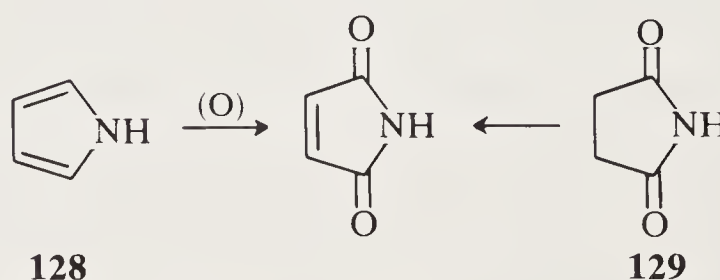


Another approach to maleimides involves protection of the maleic double bond by DA reaction.<sup>(190)</sup> Thus, 3,6-endomethylene-4-tetrahydrophthalic

anhydride **125** was prepared by the reaction of cyclopentadiene and MA. The amic acid salt **126** was obtained on treatment with ammonium hydroxide. Cyclization of **126** gave imide **127** which on thermolysis gave cyclopentadiene and maleimide. The former can be recycled to make the process efficient. The yields were high in many cases, further suggesting that low yields obtained on direct reaction are due to double-bond participation—either by addition or by isomerization. Similarly, furan adducts may be employed.<sup>(287)</sup>

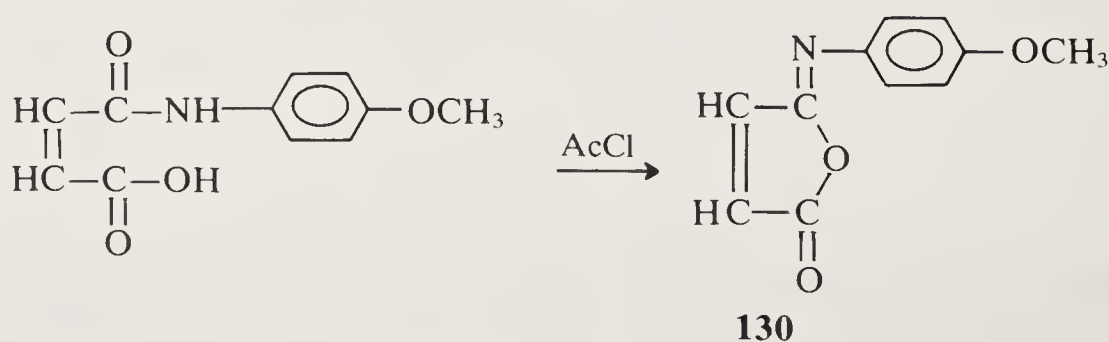


In addition to these, maleimide can also be prepared by chromic acid oxidation of pyrrole **128**,<sup>(192)</sup> or catalytic oxydehydrogenation of succinimide **129**.<sup>(193)</sup>



In an Exxon patent,<sup>(207)</sup> the reaction of isocyanate with MA to produce substituted maleimides has been claimed, although no specific examples were given.

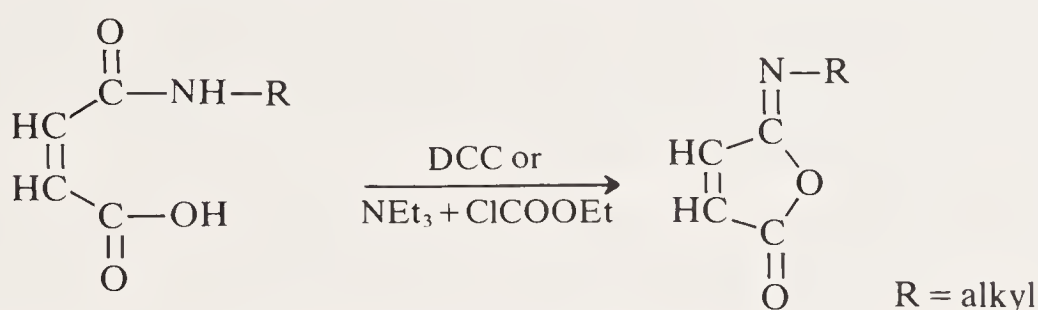
The cyclization of amic acid does not always give the imide. Acetyl chloride was reported to cyclize *p*-methoxymaleanilic acid to the isomaleimide derivative **130**.<sup>(194,195)</sup> Product **130** can also be obtained using perchloric acid



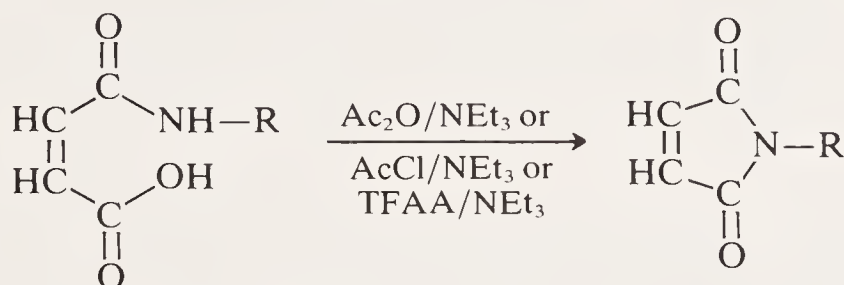


with acetic anhydride.<sup>(285)</sup> Roderick<sup>(186)</sup> employed acetyl chloride but assigned maleimide structure to the product. A number of workers have examined the effect of various dehydrating agents to classify these for selectivity to maleimide or isomaleimide.

Cotter *et al.*<sup>(196)</sup> have examined the dehydration of *N*-alkylmaleamic acids and observed that isomaleimide was the product when using either ethyl chloroformate/triethylamine or *N,N'*-dicyclohexylcarbodiimide (DCC).



On the other hand, acetic anhydride/triethylamine or acetyl chloride/triethylamine or TFAA/triethylamine gave symmetrical maleimide.



Akiyama and coworkers<sup>(164,197)</sup> have examined the ring closure of *N*-benzyloxy and *N*-hydroxymaleamic acids. Thionyl chloride and  $\text{P}_2\text{O}_5$  gave isomaleimides. With other reagents side reactions occurred without any ring closure. Ivanov has reported  $\text{P}_2\text{O}_5$  to yield maleimide from *N*-hydroxymaleamic acid.<sup>(198)</sup>

Hedaya *et al.*<sup>(199,200)</sup> have examined the reaction of bisimides and isoimides from hydrazine and hexamethylenediamine. Spectral assignments and properties have been discussed. Monoimides from hydrazine and substituted hydrazines have been studied by Dunkels and Hillers<sup>(177)</sup> and Kozinskii and Burmistrov<sup>(182)</sup> Rubinstein *et al.*<sup>(280)</sup> found a 2:1 mixture of maleimide and isomaleimide on acetic anhydride dehydration of the maleamic acid from 1,1-dimethylhydrazine and have questioned some previous structural assignments.

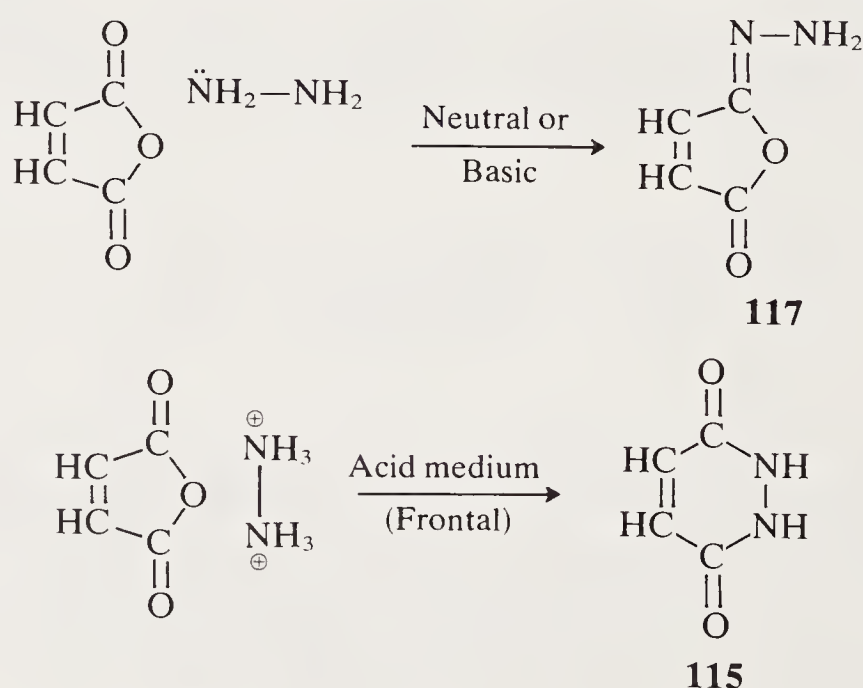
More importantly, it has been observed that isomaleimides can be rearranged to the corresponding symmetrical maleimide. Cotter *et al.*<sup>(196)</sup> have shown  $\text{NaOAc}/\text{Ac}_2\text{O}$  combinations to be effective, while Narita *et al.*<sup>(164)</sup> have also utilized various reagents. The ease with which this isomerization proceeds<sup>(196)</sup> has led Cotter and coworkers to propose isomaleimide as an intermediate for cyclization reaction.

The foregoing explains the relatively high yields of *N*-arylmaleimide obtained from the corresponding *N*-arylmaleamic acids with  $\text{Ac}_2\text{O}/\text{NaOAc}$ ,

since any isomaleimide formed would rearrange readily. Isomaleimides could also rearrange to maleimides with basic buffers,<sup>(284)</sup> acids,<sup>(164)</sup> etc., suggesting that isomaleimide is a kinetically controlled product.<sup>(280)</sup>

Thus, significant advances have been made toward obtaining maleimides and isomaleimides in the last 15–20 years. However, reports of same reagents giving different products can be found. This is further compounded by some questionable assignments in the past works which have been refuted.<sup>(164,199,280)</sup> In many cases, yields are modest and the fate of the remaining material unknown. In light of this, no generalized reagent for one or the other could be offered. Furthermore, the electronic effects could modify the course of the reaction<sup>(164,280)</sup> or prevent the cyclization.<sup>(286)</sup>

Dunkels and Hillers,<sup>(177)</sup> studying the reaction of MA with hydrazine, have proposed different modes of attack depending on the medium.



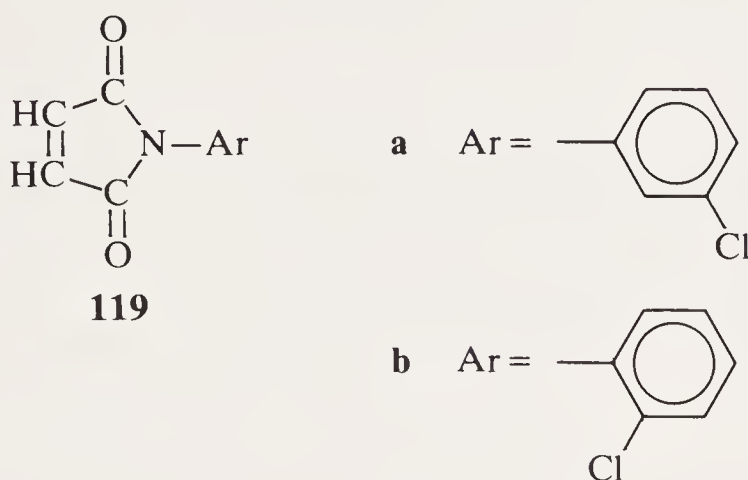
However, it appears unlikely that both the nitrogens would attack simultaneously as in the frontal attack. Thus, most of the confusion can probably be explained by the intermediacy of isomaleimide derivatives. The rate of rearrangement may then be dependent upon the nature of the substituents, medium, and catalyst—explaining the variety of results obtained with similar conditions. Suffice it to say that during the synthesis of isomaleimide or maleimides caution should be exercised in the identification of products. For example, in some experiments with low yields of the product, the fate of the remaining starting material is not clarified.

Maleamic acids have been suggested in the application for synthetic drugs. Daudon *et al.*<sup>(161)</sup> describe *N*-hydroxymaleamic acid as having bactericidal and fungicidal properties. Liu *et al.*<sup>(201)</sup> have used them as intermediates for the synthesis of potential hypocholesteremic aspartyl derivatives. Maleamic acids and derivatives have found applications as surfactants,<sup>(202,203)</sup> corrosion inhibitors, herbicides,<sup>(164,203)</sup> and resins.<sup>(25)</sup> The simple treatment of MA with amine to obtain color improvement in *N*-alkyl-1,3-propane diamines<sup>(204)</sup>



and for hardening of gelatin in photographic applications<sup>(205)</sup> involves these reactions. Aminimide derivatives have been employed as comonomers for pressure-sensitive adhesives and surfactants.<sup>(276,277)</sup>

Maleimides have found a variety of applications.<sup>(25)</sup> Augustine *et al.*<sup>(159)</sup> have reported *N*-(*m*-chlorophenyl) maleimide **119a** and *N*-(*o*-chlorophenyl) maleimide **119b** to be active as fungicides.



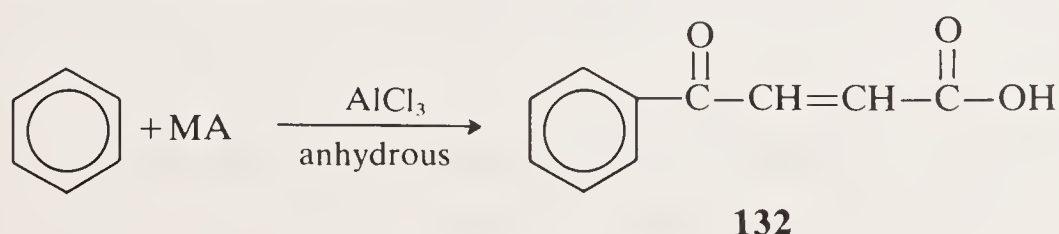
In a study involving anticancer activity, El-Merzabani and Sakurai<sup>(208)</sup> found some maleimides to be toxic rather than cytotoxic. Insecticidal properties of maleimides are known.<sup>(152)</sup>

One of the most important uses of maleimides is in the polymer field.<sup>(197)</sup> (Also see Chapters 10 and 12.) Polymaleimides are known for their temperature stability (Chapter 8). Crosslinking bismaleimide monomers are available commercially. Maleimides are also good dienophiles and hence avail themselves for DA reaction either as a reactant or a monomer for grafting. Thiols also add readily across maleimides, opening this avenue for crosslinking and grafting.<sup>(209)</sup>

### 3.4.5. Friedel–Crafts Reaction

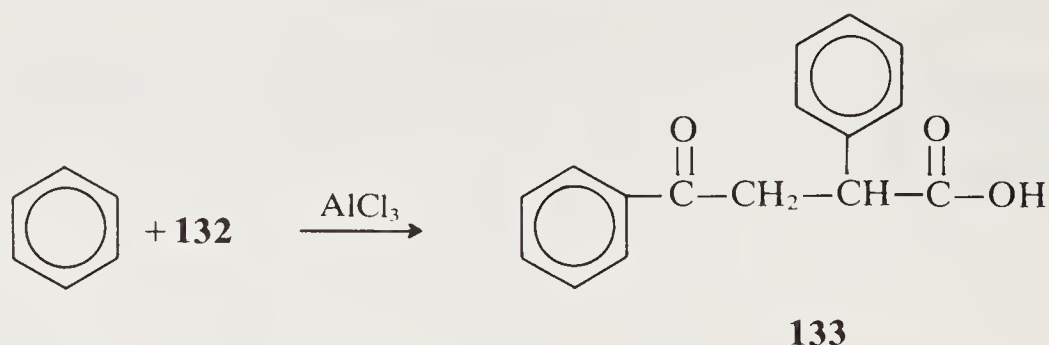
#### 3.4.5.1. Aromatics

In the presence of Lewis acid catalysts, MA can be used to acylate an aromatic nucleus; as a consequence benzoylacrylic acid **132** is formed from benzene.<sup>(210,254)</sup> Von Pechmann<sup>(210)</sup> can be credited for first observing this reaction with MA. Since then, a number of studies using MA have been published and the work has been reviewed.<sup>(211,212)</sup>

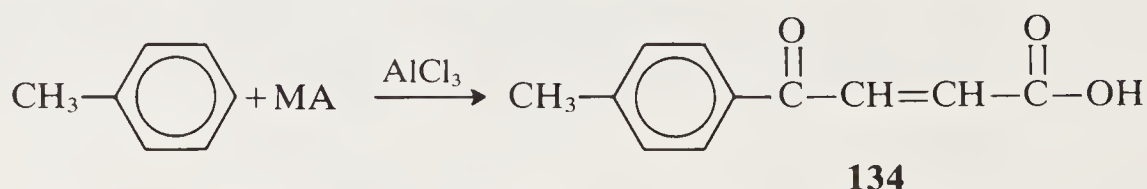




If an excess of  $\text{AlCl}_3$  is present in the reaction with benzene, the latter can further react with the product **132** to give **133**.<sup>(253)</sup>



Substituted benzene derivatives yield the corresponding  $\beta$ -aroylacrylic acids. Thus, toluene gives only the *p*-substituted product **134**.



As shown in Table 3.13, a variety of alkylbenzenes have been reacted to obtain good yields of  $\beta$ -aroylacrylic acids. In many cases, excess of the

Table 3.13. Friedel–Crafts Reaction of MA with Aromatic Compounds<sup>a</sup>

Aromatic compound	Product <sup>b</sup>	Yield (%)	Reference
Benzene	A	80–91	238, 253
	B	16	252
Toluene	A (Ar = 4-tolyl)	65–77	238
	B (Ar = 4-tolyl)	20	241, 252
Isopropylbenzene (cumene)	A (Ar = 4-isopropyl phenyl)	55	238
<i>o</i> -xylene	A (Ar = 3,4-dimethylphenyl)	76	220
<i>m</i> -xylene	A (Ar = 2,4-dimethylphenyl)	91	220
<i>p</i> -xylene	A (Ar = 2,5-dimethylphenyl)	89–90	220
Phenylcyclohexane	A (Ar = 4-cyclohexylphenyl)	68	238
1,2,4-trimethylbenzene	A (Ar = 2,4,5-trimethylphenyl)	80	220
Mesitylene (1, 3, 5)	A (Ar = 2,4,6-trimethylphenyl)	83	220
Diphenylmethane	Diphenylmethane-4,4'-oxocrotonic acid	46–58	222
Bibenzyl	Bibenzyl-4,4'-oxocrotonic acid	58–70	222
Naphthalene	A (Ar = 1-naphthyl or 2-naphthyl)	24–32	218, 240
		48	254
Acenaphthene	A (Ar = 3-acenaphthyl)	42–48	255
		32	

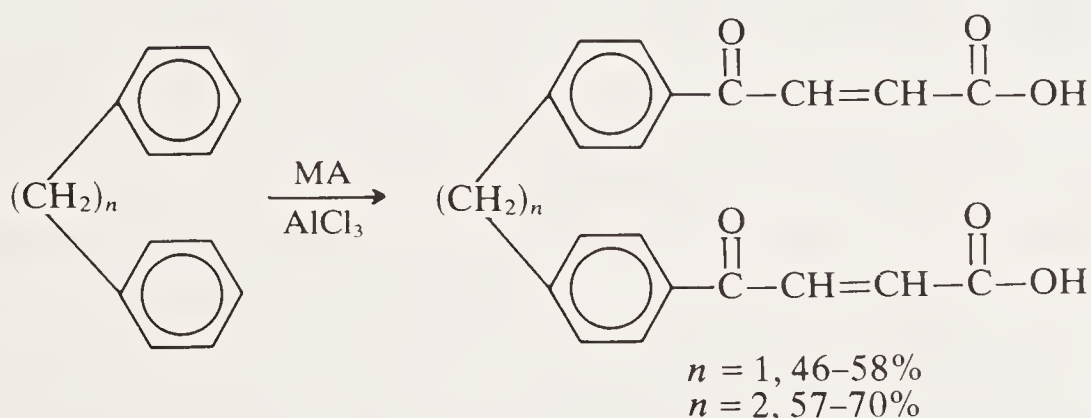
<sup>a</sup> From Reference 212.

<sup>b</sup> Products: A-type, **132**:  $\text{Ar}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}=\text{CH}-\text{CO}_2\text{H}$ ; B-type **133**:  $\text{Ar}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2-\underset{\text{Ar}}{\text{CH}}-\text{CO}_2\text{H}$

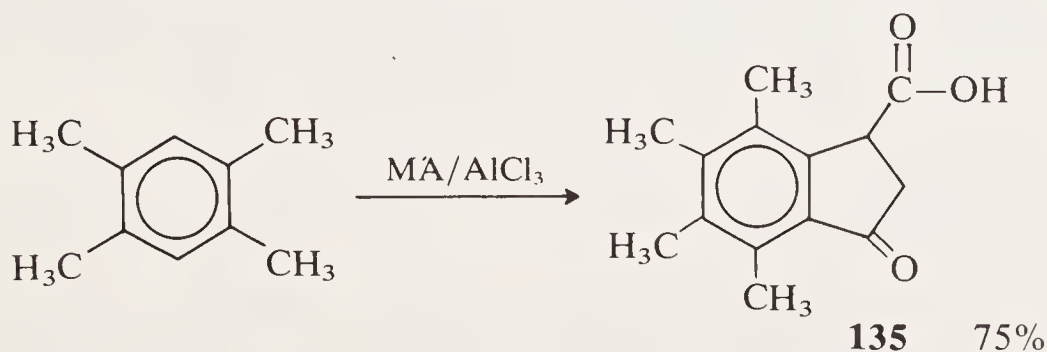
aromatic reactant has been employed as a solvent. Fieser and Fieser<sup>(213)</sup> have demonstrated that the use of tetrachloroethane as a solvent gives better yields of the products. Similar conclusions have also been reached by Abdul Sattar *et al.*,<sup>(214)</sup> using *o*-, *m*-, and *p*-chloroanisoles.

Before approaching the generality of the reaction, it may be remembered that of the two isomers, i.e., *cis* and *trans*- $\beta$ -benzoylacrylic acids, *trans* is the generally observed product.<sup>(211,212,215-221)</sup> The *trans* acids are usually yellow, while *cis* acids are white.<sup>(212)</sup>

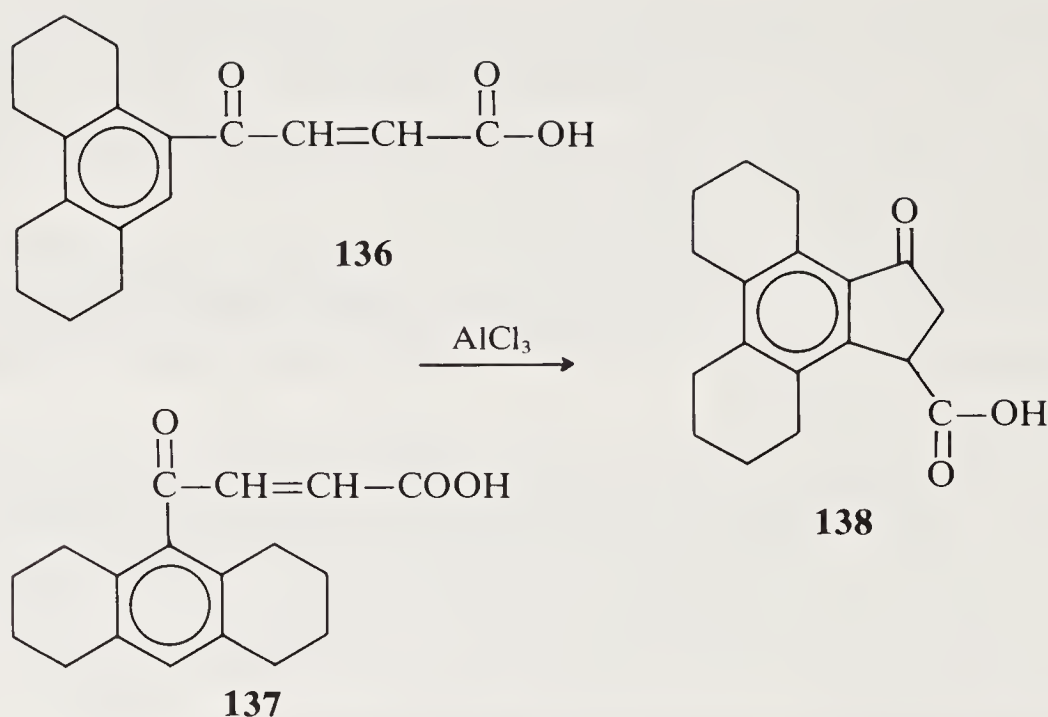
Koga<sup>(222)</sup> has shown that by using diphenylmethane and 1,2-diphenylethane, modest yields of the *p,p'*-disubstituted products also can be obtained. Since the reaction was run using excess  $\text{AlCl}_3$  and the yields are modest, one wonders about the contribution by products analogous to **133**. Among the solvents tried were chlorinated hydrocarbons,  $\text{CS}_2$ , and nitrobenzene. The best yields were obtained using 1,2-dichloroethane.



When dealing with polyalkylaromatic hydrocarbons, rearrangement of the substituents has been known to occur. Heilbrunn and Marechal<sup>(223)</sup> have shown that when durene is reacted with MA in the presence of  $\text{AlCl}_3$ , a 75% yield of the indanone carboxylic acid **135** is obtained. Thus, both acylation as well as alkylation by the anhydride and olefin fragments of MA occur.



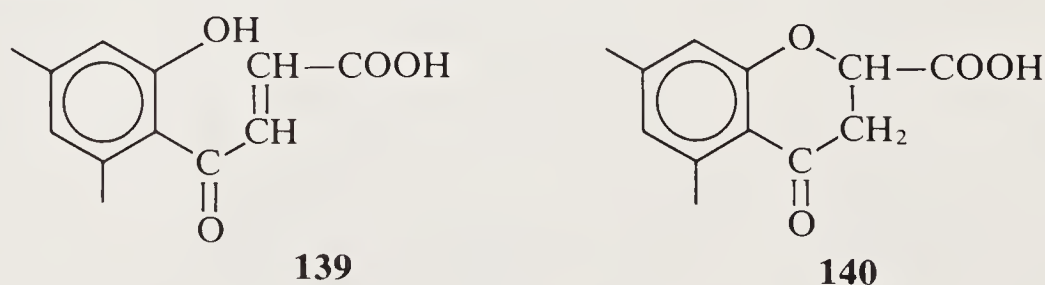
Baddeley and Williamson<sup>(224)</sup> have also shown that, when using either of the starting materials **136** or **137**, the same product of cyclization **138** is obtained. This too must involve rearrangement of the alkyl substituents around the aromatic nucleus. The *trans* geometry of the initial acylation products obtained in these and above cases may avail the preferential closing of the five-membered ring.



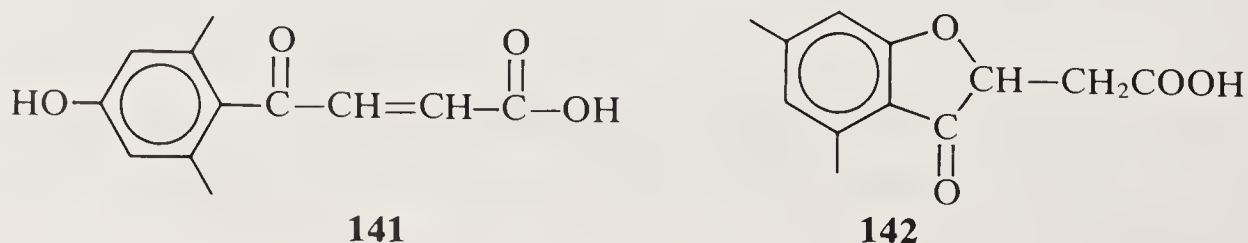
Substituted aromatic compounds have been studied and, in almost all cases, the expected benzoylacrylic acid derivative is the main product, as shown in Table 3.13. The cases of phenols and that of resorcinol and its dimethyl ether reactions are exceptions and are discussed at length to exemplify the nature of the alternate reactions.

Phenol and its derivatives are known to form phthaleins with phthalic anhydrides and the products are very well known acid-base indicators.<sup>(225)</sup> With maleic anhydride, a variety of phenols have been examined by Webster and Kamstra,<sup>(226)</sup> including halogenated phenols and aminophenols while using anhydrous stannic chloride and sulfuric acid as catalysts.<sup>(227,228)</sup> Although indicator properties of some were shown, no rigorous structure proof or yield data were given. Maleins **146** were reported to have formed.

Barr *et al.*<sup>(229)</sup> and Baddeley *et al.*<sup>(220)</sup> have examined a number of substituted phenols using anhydrous aluminum chloride catalyst. Baddeley *et al.*<sup>(220)</sup> obtained two acids from 3,5-dimethylphenol and MA. These were

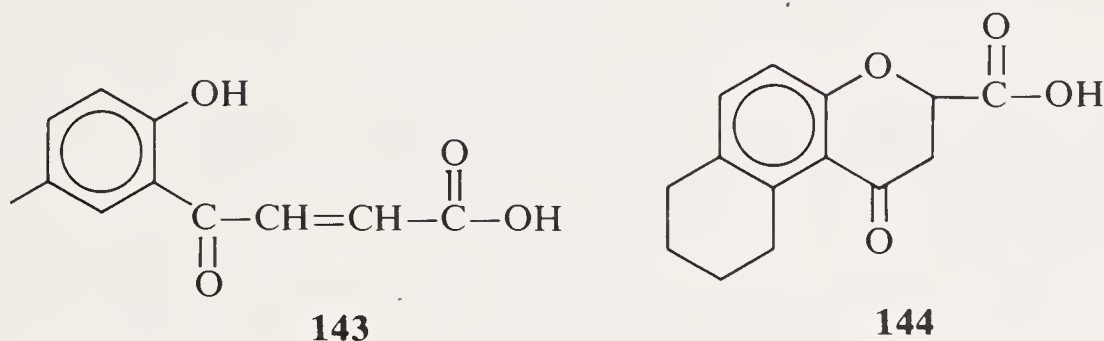


assigned the following structures **139** and **140**. However, Barr and co-workers<sup>(229)</sup> on reexamination of the reaction assigned structure **141** to the yellow product formerly assigned **139** and **142** to what Baddeley *et al.*

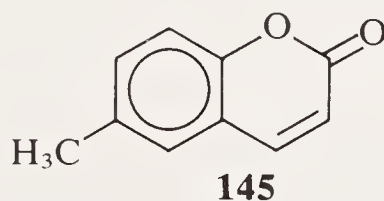




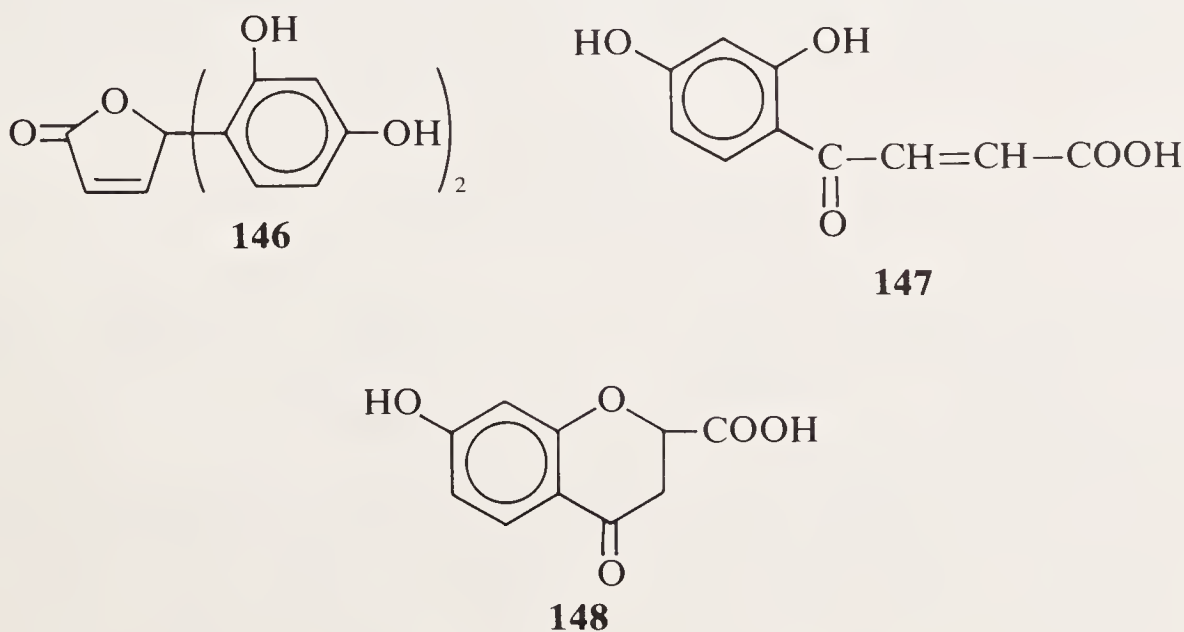
designated as **140**, which was colorless. Since **141** was shown to undergo cyclization with the  $\text{AlCl}_3$  catalyst, Barr *et al.*<sup>(229)</sup> proposed that migration of the acyl group of **141** to the *ortho* position occurred, followed by cyclization forming **142**. However, structures of type **139** are isolated from the reaction of *p*-cresol which gives **143**. Further,  $\beta$ -naphthol gave the chromanone derivatives **144**, as the only product using an aluminum chloride catalyst.<sup>(229)</sup> On



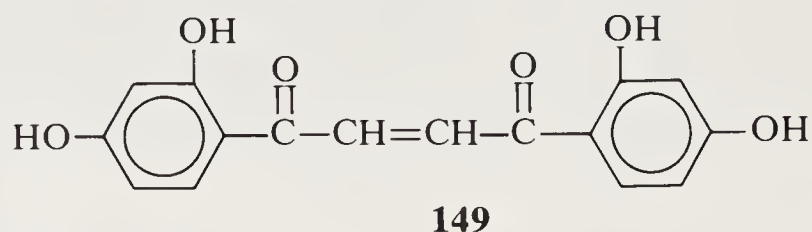
the other hand, *p*-cresol with maleic acid in the presence of 72% sulfuric acid reportedly gives an 80% yield of 6-methylcoumarin **145**.<sup>(230)</sup> Note that both formations **144** and **145** require oxidation. These variations make generalization difficult.



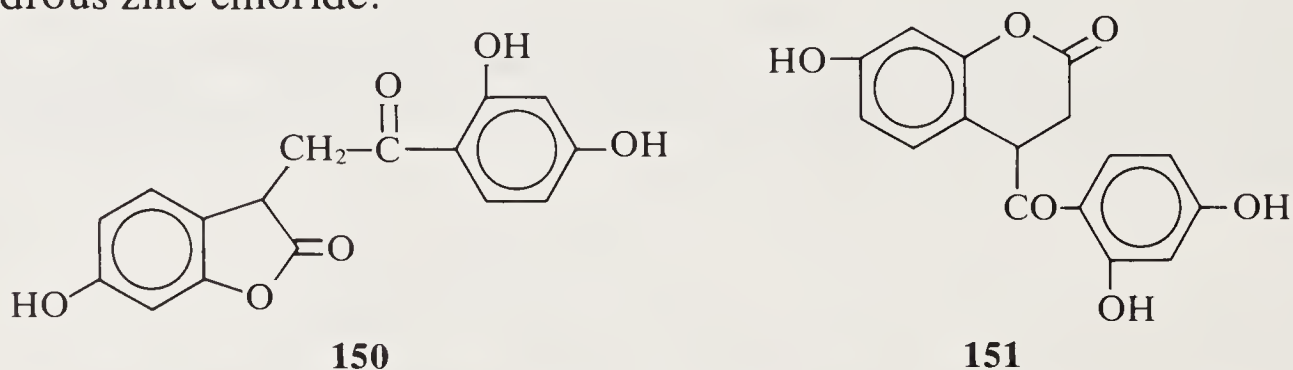
Resorcinol in particular has attracted a lot of attention. It was seen earlier that Webster and Kamstra<sup>(226)</sup> isolated a product and identified it as a malein **146** on reaction of resorcinol with MA in the presence of a stannic chloride (anhydrous) catalyst. Other workers have employed various conditions and catalysts. For example, Graff *et al.*<sup>(231)</sup> claim that the same product is obtained upon simple heating of the reactants. In the presence of anhydrous aluminum chloride, Barr *et al.*<sup>(229)</sup> obtained two products, namely,  $\beta$ -2,4-dihydroxybenzoylacrylic acid **147** and chromanone derivative **148**. The latter is produced



by the cyclization of the former. No mention of a 2 : 1 resorcinol : MA product such as a malein was made. Rao *et al.*<sup>(232)</sup> have reportedly obtained a small amount of malein **146** in addition to the 1,4-diketone **149** as the major product

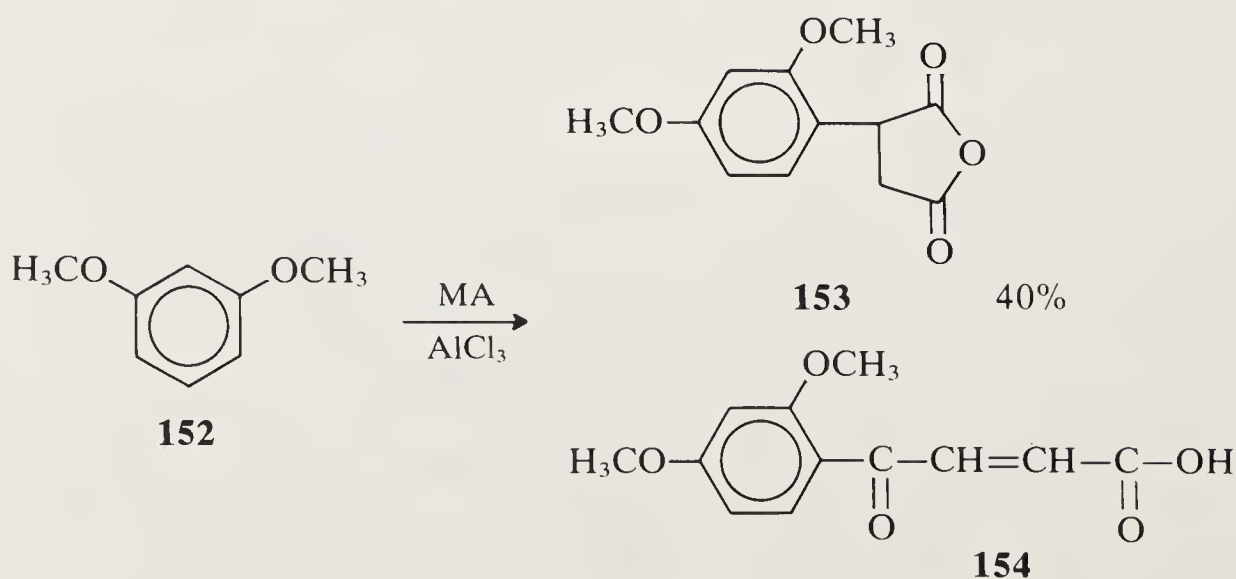


using anhydrous zinc chloride catalyst. Bird and Molton<sup>(233)</sup> claimed to have isolated a lactone **150** in the presence of  $\text{H}_2\text{SO}_4$ . They rejected the malein structure proposed by Webster and Kamstra<sup>(226)</sup> obtained using  $\text{SnCl}_4$  and that obtained by Graff *et al.*<sup>(231)</sup> by the action of heat alone. Molyneaux and Jurd<sup>(234)</sup> claimed having obtained product **151** from resorcinol and MA using anhydrous zinc chloride.



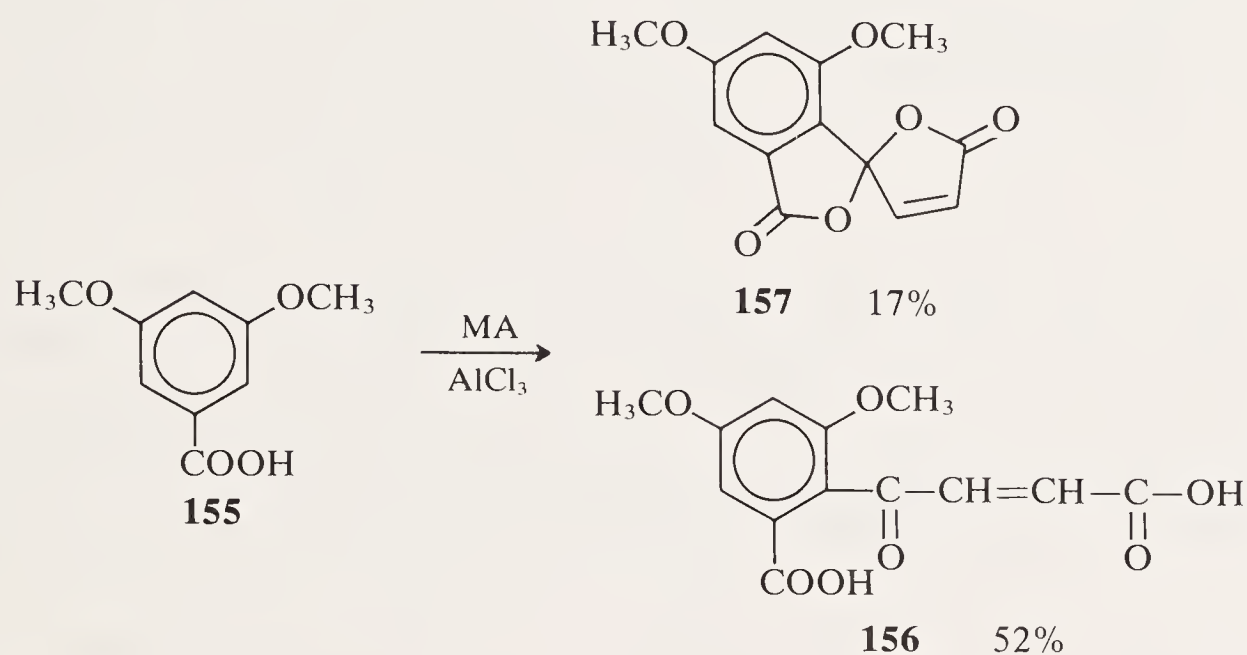
Recently, however, Molyneaux<sup>(235)</sup> has made an attempt at solving this confusion. On reexamination of the reaction, and by alternate synthesis of the derivatives and studying their NMR spectra, he has established that the 2 : 1 resorcinol : MA product is really 3-(2',4'-dihydroxybenzoyl-methyl)-6-hydroxybenzofuran-2-ene **150**. This does not negate formation of other products. A complete accounting of MA may be very revealing.

In contrast to the phenol derivatives, phenol ethers have been reported to give acylation with MA in the presence of  $\text{AlCl}_3$ .<sup>(211,212,214,236,237)</sup> Resorcinol dimethylether **152** is an exception, since 2,4-dimethoxyphenylsuccinic acid **153** is the major product reported by Rice<sup>(238)</sup> with small amounts of the

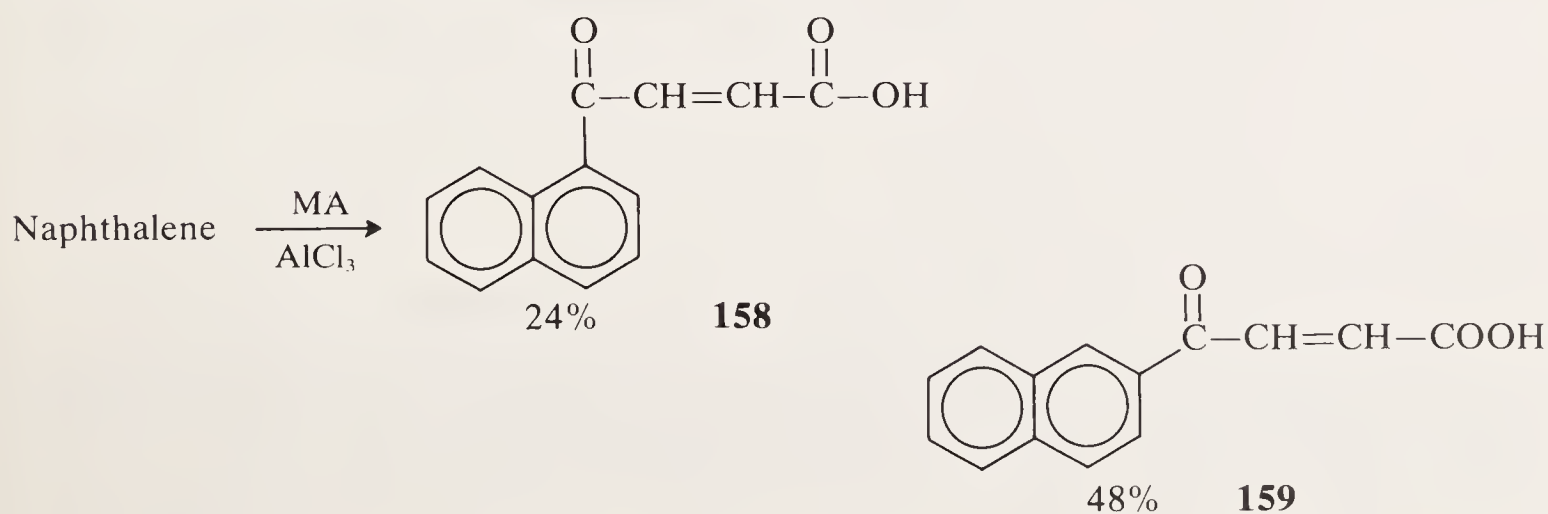


usual benzoylacrylic acid derivative **154**, employing carbon disulfide as a solvent. However, Baddeley *et al.*<sup>(220)</sup> claim **154** as the product but no yields are given. Papa *et al.*<sup>(239)</sup> on the other hand claim a 68% yield of **154** using tetrachloroethane as solvent. Both Rice and Papa give quite different melting points for their respective major products. Thus, it is not clear why, under very similar reaction conditions, different products are obtained. This chemistry needs a more systematic study including identification of all the major and minor products.

Gourmelon and Graff<sup>(240)</sup> have examined the reaction of 3,5-dimethoxybenzoic acid **155** with MA. In addition to acylation product **156**, a significant amount of the spiro compound **157** was formed. A rigorous structure proof for the products was given.

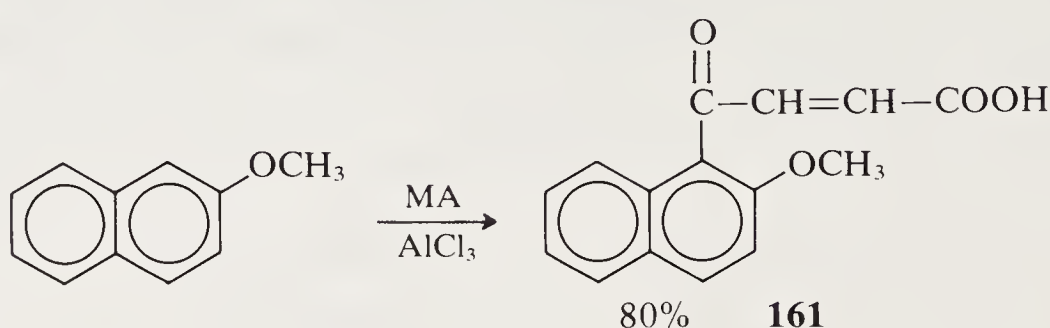
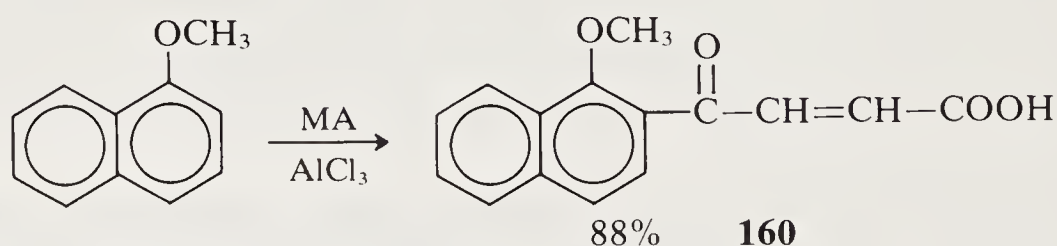


Fused aromatic systems such as naphthalene give both 1 and 2 acylation to yield  $\beta$ -1- and  $\beta$ -2-naphthoylacrylic acid.<sup>(255)</sup> Acenaphthene is converted to B-(3-acenaphthoyl) acrylic acid.<sup>(256)</sup> Side reactions such as cyclization are possible in these systems but are avoidable if the reaction is allowed to run in the absence of excess  $\text{AlCl}_3$  or undissolved  $\text{AlCl}_3$ . For naphthalene the predominance of the 2-acyl product is obtained only when a 2:1 ratio of  $\text{AlCl}_3$ :MA is employed. If less  $\text{AlCl}_3$  is used, nearly complete preference for the 1-acyl derivative can be obtained.<sup>(241)</sup>

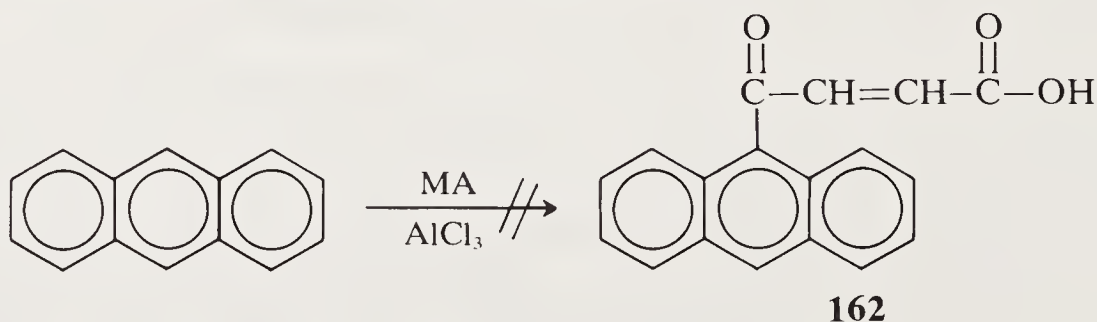




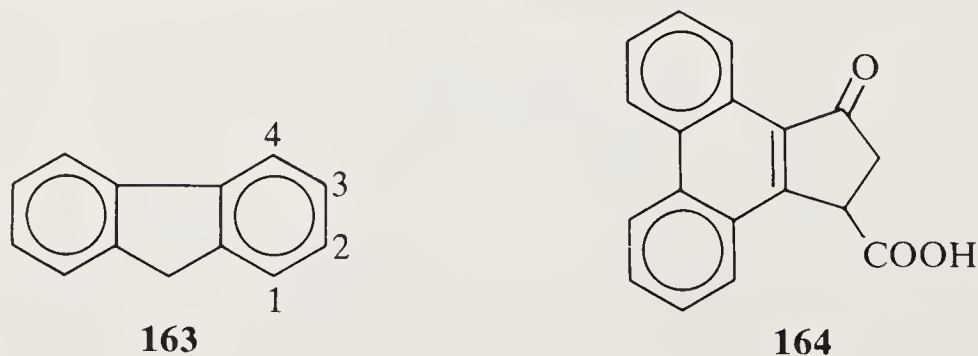
1- and 2-methoxynaphthalenes have been reported by Dave *et al.*<sup>(237)</sup> to give excellent yields of the expected acylated products. The high yields obtained by Dave *et al.* may reflect the lack of cyclization sites available on the naphthalene nucleus in the products.



Oddy<sup>(242)</sup> had claimed that anthracene yielded a  $\beta$ -9-anthroylacrylic acid **162**. This is highly questionable since Yates and Eaton<sup>(243)</sup> have shown that the Diels–Alder reaction of MA with anthracene can be accelerated using anhydrous  $\text{AlCl}_3$ . Thus, probably the product obtained by Oddy<sup>(242)</sup> was either the DA adduct or a product derived therefrom.



Kretov and Lutrinov<sup>(245)</sup> have shown that high yields of the 2-acyl derivative can be obtained from fluorene **163** and MA. If the 2 positions are occupied by other substituents, MA may react in the 3 position.<sup>(244)</sup>



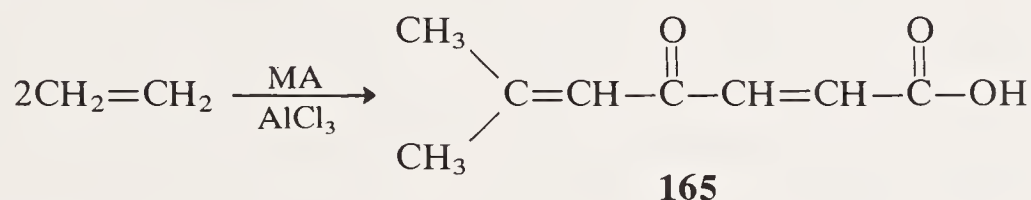
Phenanthrene has been shown to give a low yield of the cyclized product **164** by DeWalt *et al.*<sup>(246,247)</sup> The latter had used  $\text{AlCl}_3$ /MA molar ratio of 3.3:1. Since a large excess of  $\text{AlCl}_3$  is known to promote side reactions, this

reaction may give higher yields in the presence of an optimum amount of dissolved  $\text{AlCl}_3$ .

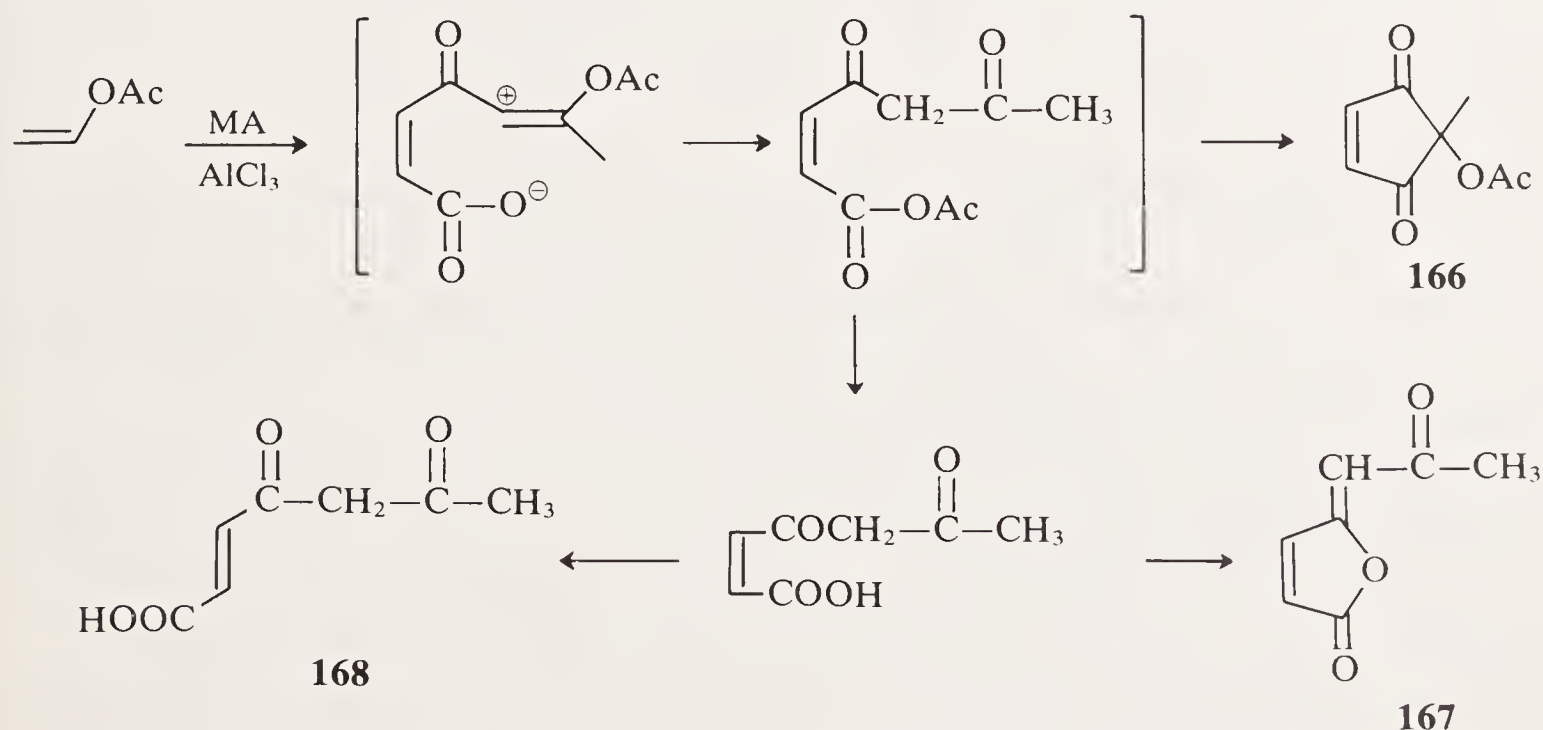
### 3.4.5.2. Olefins

The acylation of olefins with MA has not been investigated a great deal. Below are given two examples to illustrate the synthetic potential and complexities involved.

Taylor<sup>(257)</sup> attempted the reaction of MA with ethylene at 25°C. An excess of aluminum chloride was needed. Interestingly, the reaction mixture absorbed two moles of ethylene before slowing down. A 15% yield of the unsaturated keto acid **165** was obtained. Isobutylene residue in the latter may reflect isomerization of a carbonium intermediate. No by-products were explored but if dimerization precedes acylation, contributions by ene reaction and polymerizations cannot be ruled out.



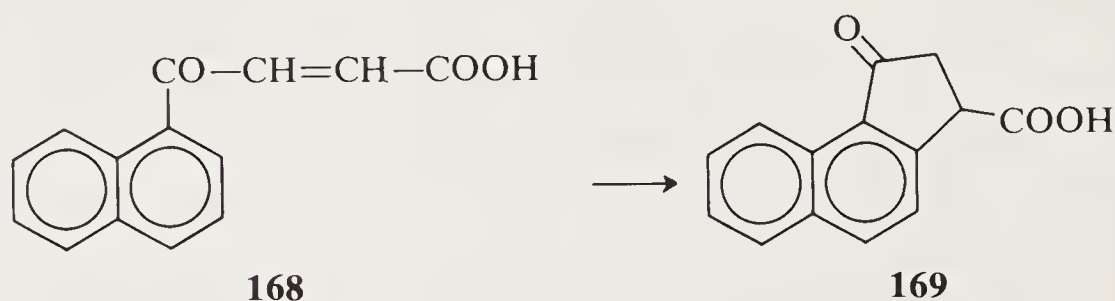
Nilsson<sup>(248)</sup> has reported the reaction of isopropenyl acetate with MA. Products including **166**, **167**, and **168** were obtained. A mechanism for their formation was proposed as follows:



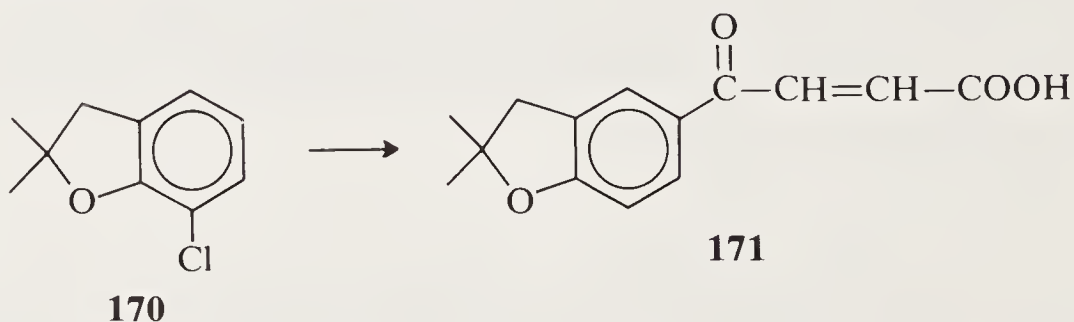
The nature of products in these examples suggests very complex reactions between MA and olefin under Friedel–Crafts conditions. Furthermore,  $\text{AlCl}_3$  may catalyze the ene reaction also increasing the product complexities. However, a detailed product study may reveal the nature of competitions and intermediates involved.

### 3.4.5.3. Uses

The Friedel–Crafts reaction of MA with aromatic compounds has many varied applications. The number of reactive centers available makes these derivatives an easy choice as intermediates. For example, the ring closure of naphthalene derivatives **158** and **159** gives the starting point for a steroid nucleus since the B-, C-, and D-ring framework is easily accessible.



Recently, Hirose *et al.*<sup>(249)</sup> have obtained 74% yield of **171** by acylating 7-chloro-2,2-dimethyl-2,3-dihydrobenzofuran **170** with MA in the presence of  $\text{AlCl}_3$ . The compound was evaluated with other structurally analogous compounds for anti-inflammatory action. Compound **171** showed high gastric irritation in their study.

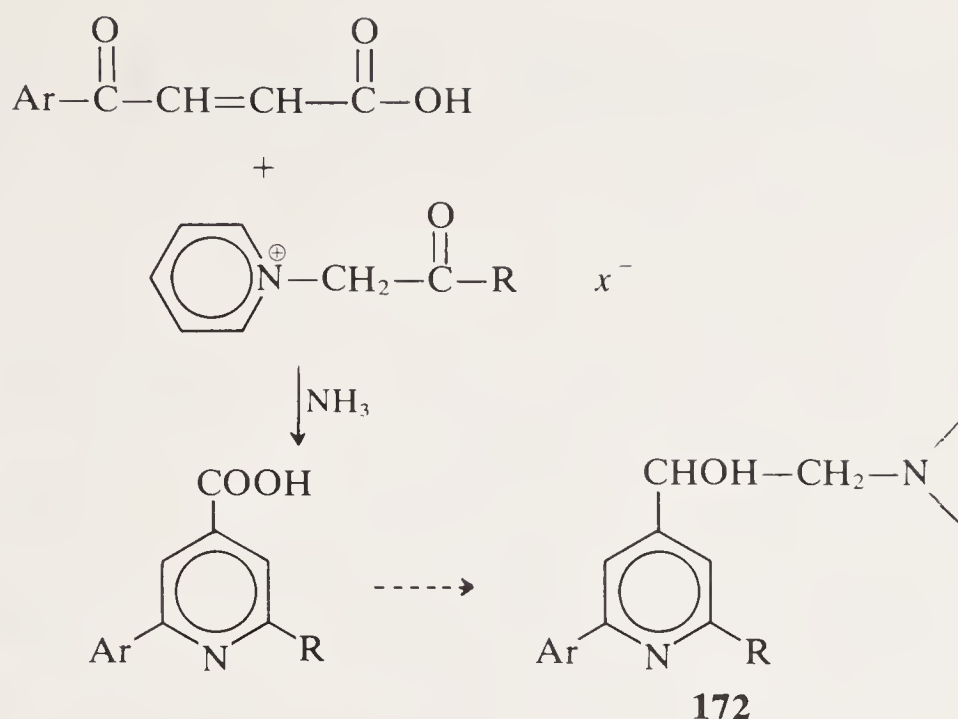


As seen in the case of phenols from the works of Baddeley *et al.*,<sup>(220)</sup> Barr *et al.*,<sup>(229)</sup> and Ziegler *et al.*,<sup>(250)</sup> cyclization of  $\beta$ -2-hydroxy-benzoylacrylate gives chromanone or coumarinone derivatives depending on the structure of the phenolic unit. This possibility provides an important approach to the synthesis of chromone and coumarin derivatives.

Ash *et al.*<sup>(251)</sup> have employed the Friedel–Crafts reaction of aromatic compounds with MA and reactions of the product to obtain a pyridine nucleus. The sequence of reactions below shows their approach to the synthesis of derivatives **172**. These compounds have been claimed as antimalarials.

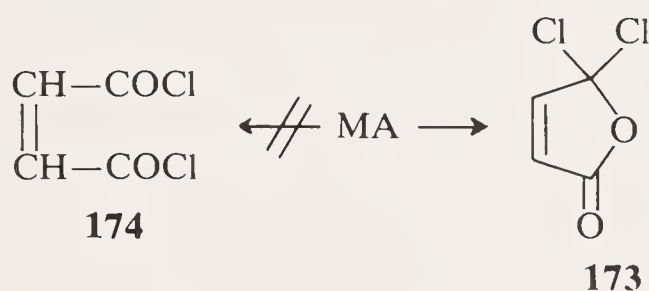
In addition, the structure  $-\text{CH}=\text{CH}-\text{CO}-$  has been found to be common to penicillic acid and claracin antibiotics leading Geiger and Conn<sup>(252)</sup> to propose that antibacterial activity may be closely associated with this grouping. The latter, as can be seen, is easily achieved with MA through the Friedel–Crafts reaction. The stereochemistry of the acids is usually *trans*. These have been known to form Pechmann's dyes.<sup>(211,212)</sup>





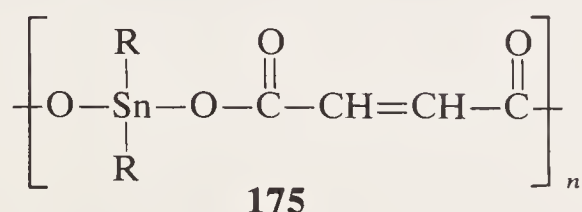
### 3.4.6. Acid Chlorides of MA

The monoacid chlorides of maleic acid and fumaric acid are not known. On treatment with reagents such as phthaloyl chloride, phosphorus pentachloride, or thionyl chloride, MA gives “maleyl chloride” **173**.<sup>(258)</sup> Maleic acid behaves similarly. The noncyclic maleoyl chloride **174** is also not known. Fumaric acid, however, can be converted to fumaroyl chloride in high yields with conventional reagents.<sup>(258,259)</sup> Compounds such as this are potential intermediates.

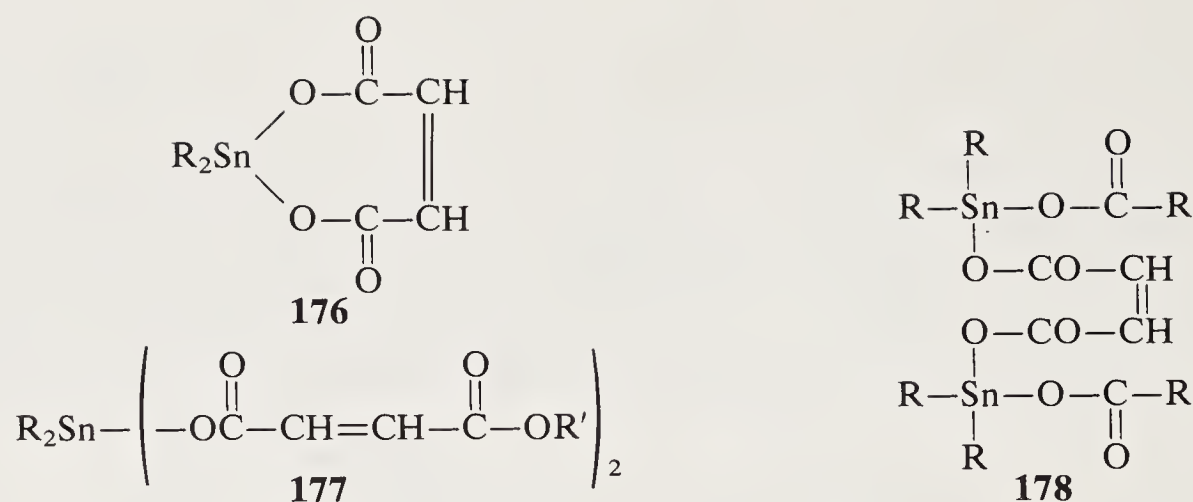


### 3.4.7. Metal Compounds

A composition of dibutyltin maleate **175** was proposed as a vinyl stabilizer.<sup>(264)</sup> The product was subject to further polymerization due to



unsaturation.<sup>(265)</sup> However, alkyltin maleate and fumarate compounds such as **176**, **177**, and **178** continue to generate patent activity as a stabilizer and flame retardant for vinyl halide, vinyl halide-ABS, and styrene resins.<sup>(265-271)</sup>



Compounds such as **177** and **178** may be made by the use of alkali salts of monoalkyl maleate or fumarate. This approach has been extended to include other metals such as zinc and zirconium<sup>(272,273)</sup> and these compounds are claimed to be heat stabilizers and impart transparency to vinyl resins. Compounds of a number of other metals have been studied.

### 3.5. EPILOGUE

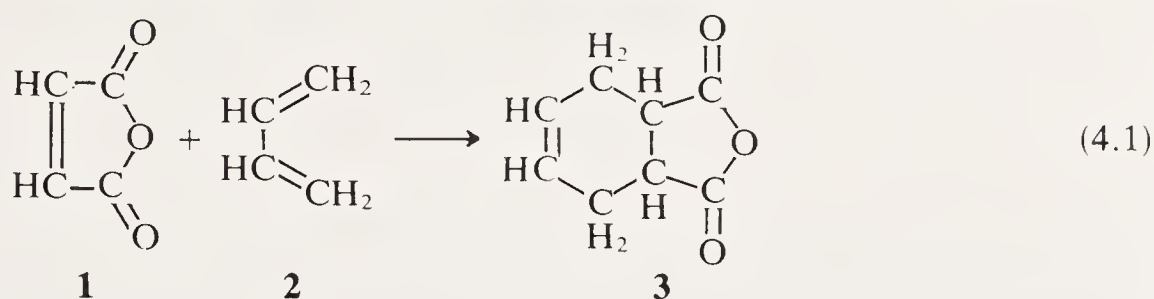
As can be seen from the foregoing, MA is a unique compound since it is both an anhydride and an olefin. Due to the possibility of independent manipulation of its functionalities, it lends itself to interesting synthetic possibilities. Some areas of its reactivity such as those highlighted by the maleimide synthesis and the Friedel–Crafts aspects need a greater systematization. Questions such as why different products are observed by different laboratories under similar conditions need to be answered. It is obvious that all the parameters affecting these reactions are far from well understood. In spite of this, the importance of products generated by the chemistry of MA has not been and should not be undermined.

# 4

## DIELS–ALDER REACTION

### 4.1. INTRODUCTION

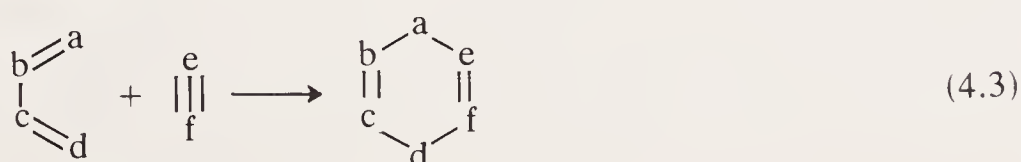
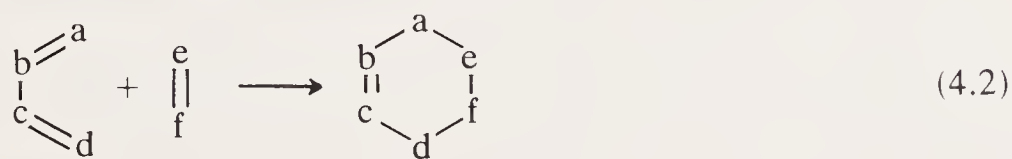
In this chapter, we will consider the one reaction of maleic anhydride that has been most investigated in the last half-century. Of historical significance is the formation of a cyclohexene derivative **3** from a conjugated diene (butadiene) **2** and a dienophile (maleic anhydride, MA) **1** as reported



by Otto Diels and Kurt Alder in 1928.<sup>(1)\*</sup> This reaction is called the Diels–Alder (DA) reaction, diene synthesis, or the [4 + 2] cycloaddition reaction. The role that MA has played in this reaction along with other dienophiles cannot possibly be covered in a single chapter such as this. The impetus it provided to synthetic organic research, particularly in the fields of steroids, polycyclic aromatics, and alkaloids, by allowing a one-step ring closure, can barely be exemplified in a treatment such as this. The efforts of Diels and Alder were duly recognized by a Nobel Prize for chemistry in 1950.<sup>(2)</sup>

### 4.2. DEFINITION

The more general cycloaddition aspect of the Diels–Alder reaction can be exemplified below wherein two bonds are expended in the reactants to generate two new bonds resulting in a ring-closed product, wherein abcd is a diene and ef is olefinic or acetylenic dienophile.<sup>(8,182)</sup>



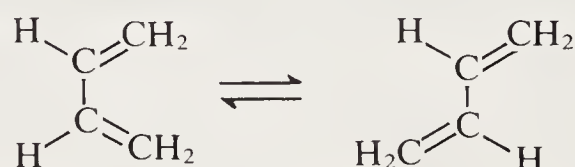
\* Although similar observation of the reaction had been made earlier, we owe it to Diels and Alder for the utility and mechanistic interpretation resulting from their classical papers.



Although our primary interest is maleic anhydride (an olefinic dienophile), we have chosen to include related aspects of the Diels–Alder reaction whenever they contribute to an understanding of the process.

The diene moiety usually contains four carbon atoms and examples are also known when the diene can be conjugated olefinic and acetylenic linkages.<sup>(7)</sup> However, the diene may contain a heteroatom, e.g., O or N, to yield a heterocyclic product.

One aspect of the Diels–Alder reaction is the crucial “cisoid” or quasicyclic<sup>(8)</sup> geometry needed in the diene for the reaction. In the acyclic system, the “cisoid” and “transoid” forms are in equilibrium through the rotation around the single bond:



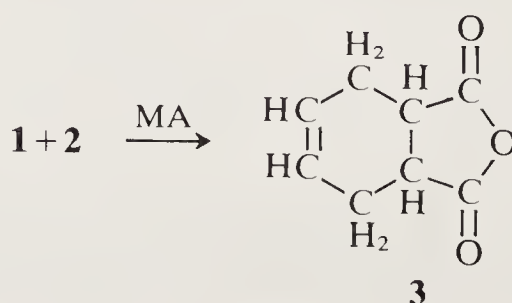
In the cyclic systems, where the geometries can be fixed due to the lack of rotation, only the cisoid forms react. In certain cases, the reaction occurs after the transoid geometry changes to cisoid through a rearrangement involving other atoms. This cisoid specificity of the DA reaction has been used as a tool for the identification of *cis* geometry of double bonds in cyclic structures.<sup>(9,23,77)</sup>

A more detailed discussion on the mechanism of the DA reaction will be included later during the chapter since certain stereochemical and retro Diels–Alder aspects will be needed for its understanding. We will first begin by exploring the scope of the reaction with various dienes.

### 4.3. SCOPE OF DA REACTION

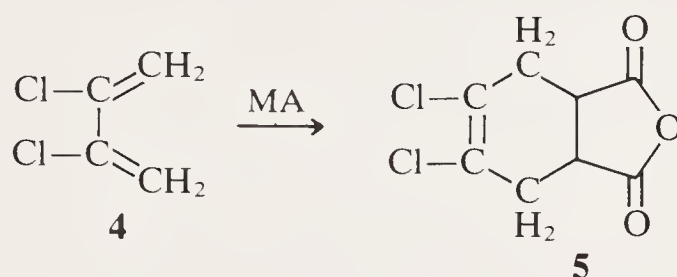
#### 4.3.1. Acyclic Dienes

In their first paper on the subject that bears their name, Diels and Alder reported the reaction of MA with 1,3-butadiene.<sup>(1)</sup> The reaction can be conducted at room temperature for 12 h to obtain quantitative yields of the tetrahydrophthalic anhydride **3**. In most cases, maleic anhydride can be replaced by its esters or other such derivatives. If other dienophiles such as



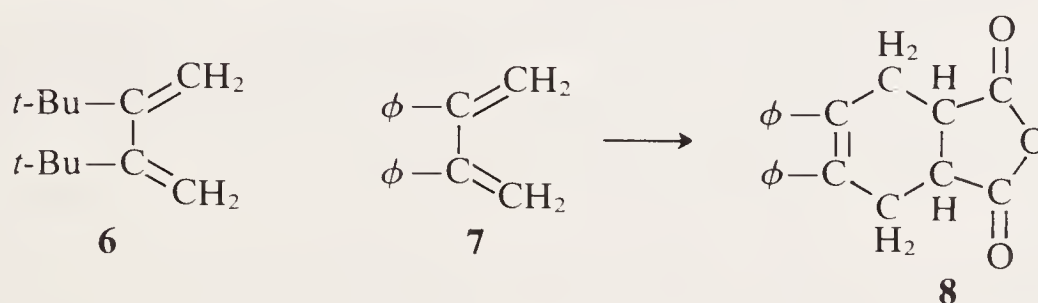
dimethyl maleate or fumarate are used, the original geometry of the dienophile is retained; i.e., maleate gives the *cis*-diester and fumarate the *trans* derivative. The same holds true for maleic and fumaric acids when reaction is possible.

Substituted butadienes also undergo addition with maleic anhydride. Isoprene and dienes substituted in the 2 and/or 3 position also undergo reaction and generally give high yields. When dealing with substituted butadienes, one should be careful in interpreting the lack of reaction. For example, Berchet and Carothers<sup>(10)</sup> have reported that 2,3-dichlorobutadiene **4** does not react with MA and the polymerization of **4** occurs. Craig *et al.*,<sup>(11)</sup> however, showed that an adduct **5** is formed in a 70% yield. Thus, the influence



of the Cl atom is not steric. As shown by Craig *et al.*,<sup>(11)</sup> chlorine substitution decreases the reactivity in butadiene. Norton's<sup>(12)</sup> report about the unreactivity of 1-chloro-1,3-butadiene has also been disputed by Craig *et al.*<sup>(11)</sup> It appears that the *cis* form does not react; however, the *trans* 1-chloro-1,3-butadiene does form an adduct. Certain halogenated dienes, which have been thought unreactive because they polymerize too readily, have also formed adducts with the help of a catalyst,<sup>(13)</sup> as will be seen later.

Steric hindrance in achieving a cisoid configuration in 2,3-di-*t*-butyl-1,3-butadiene **6** could be responsible for its lack of reactivity.<sup>(14)</sup> However, 2,3-diphenyl-1,3-butadiene **7** gives a quantitative yield of the adduct **8**.<sup>(15)</sup> Not enough steric hindrance is offered, therefore, by chlorine atoms and phenyl groups in the 2 and 3 positions.



In Table 4.1 the reactivities of some 2-substituted and 2,3-disubstituted-butadienes from the work of Craig *et al.*<sup>(11)</sup> are compared. Note that 2-alkyl substitution in each case increases the rate by facilitating a cisoid configuration. Furthermore, the larger the alkyl group, the higher the acceleration rate. Rate decrease in 2-chloro-1,3-butadiene is due to the importance of the electronic effect.

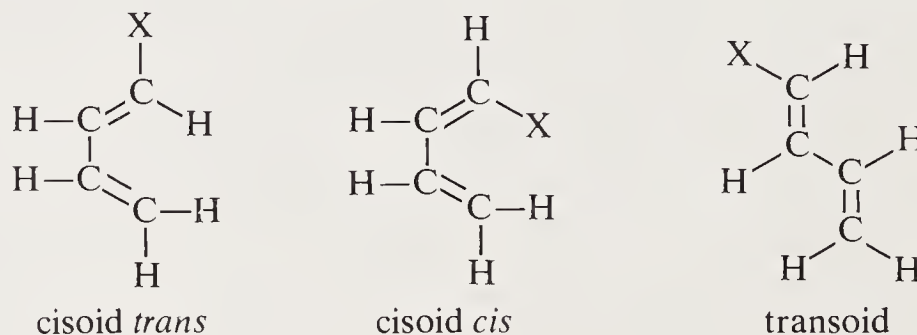
Butadienes substituted in the 1 position can exist as either *cis* or *trans* isomers. In all reported cases, the *trans* compound gives much higher yields

Table 4.1. Relative Rate of Reaction of Various Aliphatic 1,3-Dienes with MA at 25°C<sup>a</sup>

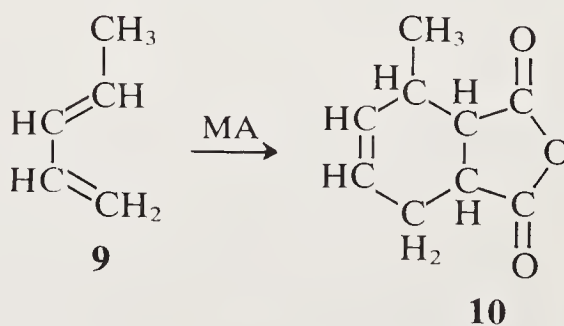
1,3-Diene	Relative rate
1,3-Butadiene	1.0
2-Methyl-1,3-butadiene (isoprene)	3.0
<i>trans</i> -1,3-Pentadiene	4.5
2-Ethyl-1,3-butadiene	5.8–6.3
2-Isopropyl-1,3-butadiene	11.6
2,3-Dimethyl-1,3-butadiene	10.6
2- <i>t</i> -butyl-1,3-butadiene	27.9–30.5
2-Neopentyl-1,3-butadiene	50.5
1-Methoxy-1,3-butadiene	31.5
2-Methoxy-1,3-butadiene	10.0
2-Chloro-1,3-butadiene	0.1
2,3-Dichloro-1,3-butadiene	0.004 7
3-Chloro-2-methyl-1,3-butadiene	0.63

<sup>a</sup> From Reference 11.

than the *cis* analog. This is because, in the *cis* derivative, formation of the cisoid structure is sterically hindered as shown below:<sup>(8)</sup>



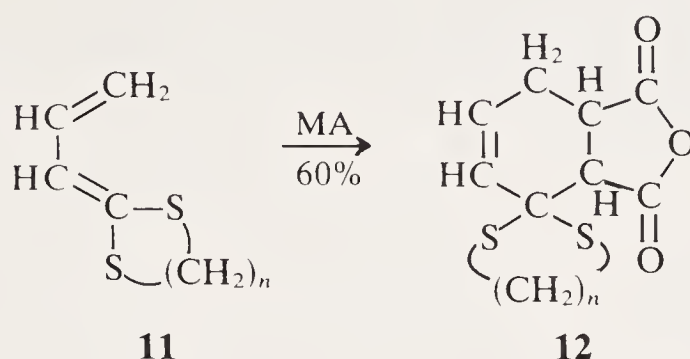
Thus, *trans*-piperylene **9** gives a near quantitative yield of the adduct **10** under conditions in which *cis*-piperylene gave no reaction. The latter does react, however, under more drastic conditions.<sup>(16)</sup>



In certain cases, 1,1-disubstituted dienes undergo adduct formation, although somewhat higher temperatures are needed. Thus, the thioacetal of

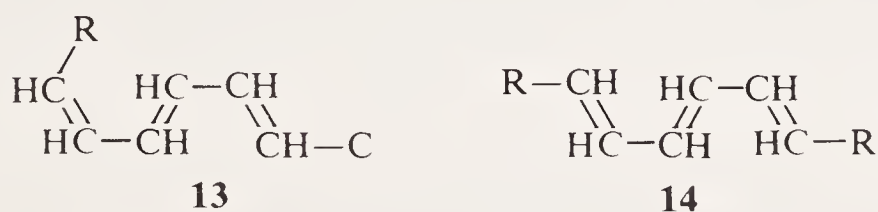


vinyl ketene **11** is known to give good yields of the adduct **12** in refluxing xylene.<sup>(17)</sup> Similarly, (trimethylsilyl) vinylketene,<sup>(226)</sup> a stable isolable ketene, gives 89% of MA adduct under mild conditions.



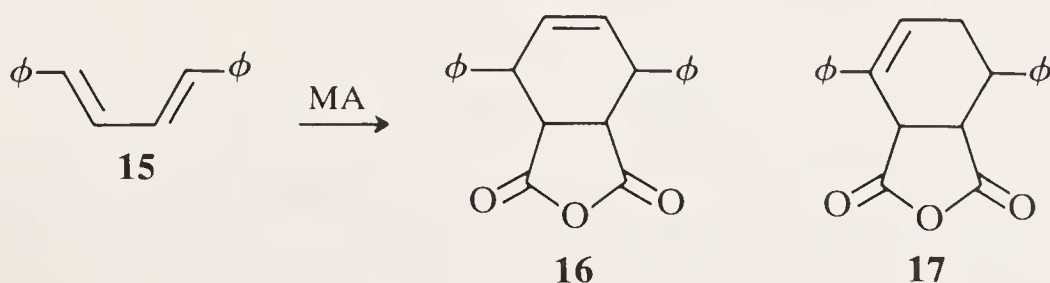
Similarly, *trans*-1-phenyl-1,3-butadiene gives, in 4 h with refluxing toluene, near quantitative yield with maleic anhydride. The *cis* isomer gives only 5% of the product.<sup>(18)</sup> Results such as this point to the importance of achieving cisoid geometry and the effect of steric hindrance on adduct formation.

A further illustration of the need for cisoid geometry may be given. Eleostearic acid, a naturally occurring trienoic acid, occurs in two forms,  $\alpha$  and  $\beta$ . The  $\alpha$  form has *cis-trans-trans* geometry **13** whereas the  $\beta$  form is all *trans* **14**.

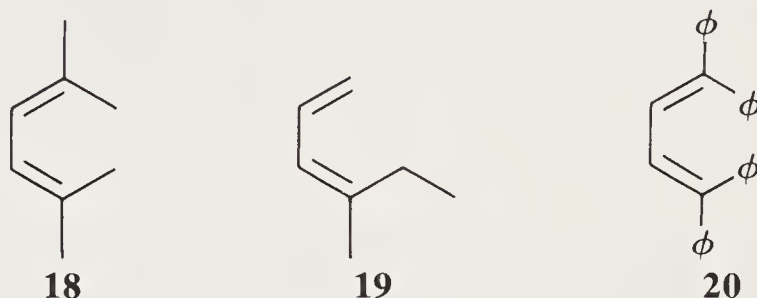


Based on considerations described so far, it can be expected that the  $\beta$  form may give two isomeric maleic anhydride adducts whereas  $\alpha$  should give only one under nonforcing conditions. Bickford *et al.*<sup>(19)</sup> by means of IR and epoxidation studies have shown that to be the case; disproving earlier conclusions that  $\beta$ -eleostearic acid adds only at the 9,11 double bond.<sup>(20,21)</sup>

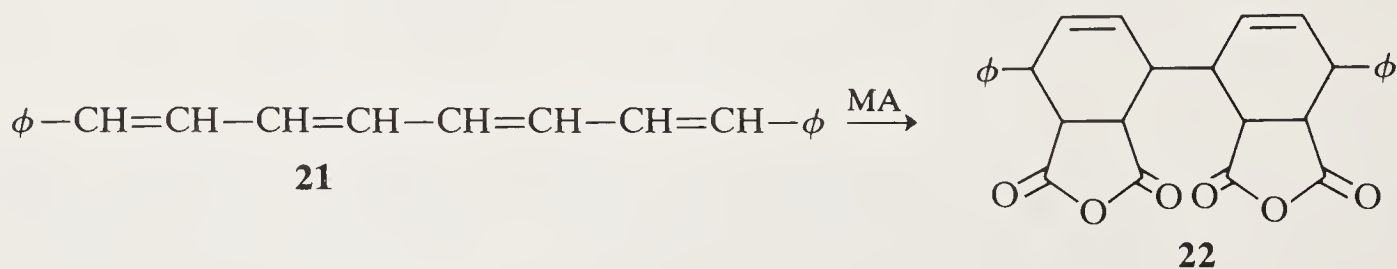
In Eq. (4.2) it is implied that the residual double bond during a diene synthesis is formed at the b-c position. Although this is true generally, often the double bond may migrate to a thermodynamically more stable position to give isomeric products. The case in point is the reaction of 1,4-diphenyl-1,3-butadiene **15** with MA. In this reaction, two isomeric products **16** and **17** are obtained.<sup>(22)</sup>



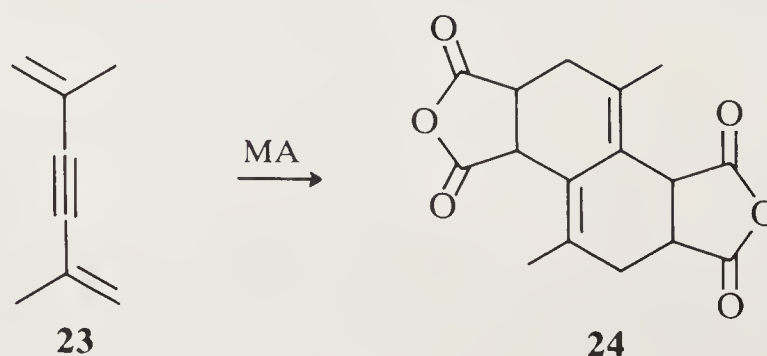
As expected, dienes with multiple substitution in the 1 and 4 positions, e.g., 2,4-dimethyl-2,4-hexadiene **18**, 4-methyl-1,3-hexadiene **19**, and 1,1,4,4-tetraphenyl-1,3-butadiene **20**, fail to react with maleic.<sup>(23)</sup> In these cases, only polymeric products are obtained. This is ascribable to the inability of the dienes to attain cisoid geometry. It must be remembered that these restrictions apply for acyclic dienes only.



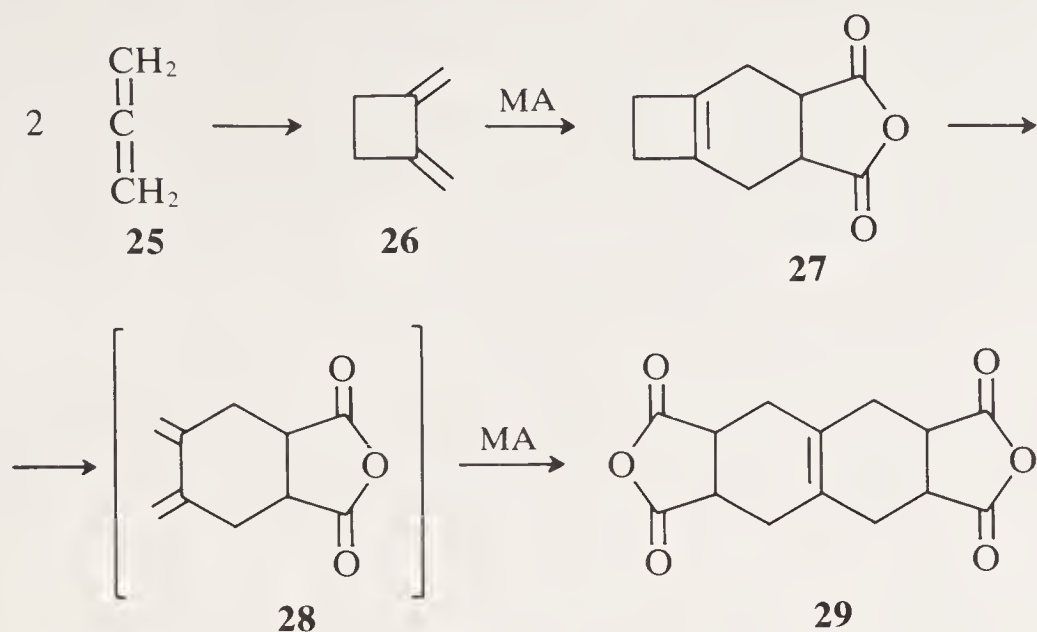
Maleic anhydride reacts with conjugated polyenes whenever a cisoid geometry can be achieved. Thus, 1,8-diphenyloctatetraene **21** adds 2 moles of MA.<sup>(22)</sup> If insufficient MA is employed, a diadduct and unreacted starting material are obtained. Thus, the second addition takes place much faster than the first one. The product **22** obtained was called "homogeneous" but the position of the double bond is uncertain. Dehydrogenation and decarboxylation of the acid from this material can yield tetraphenyl.



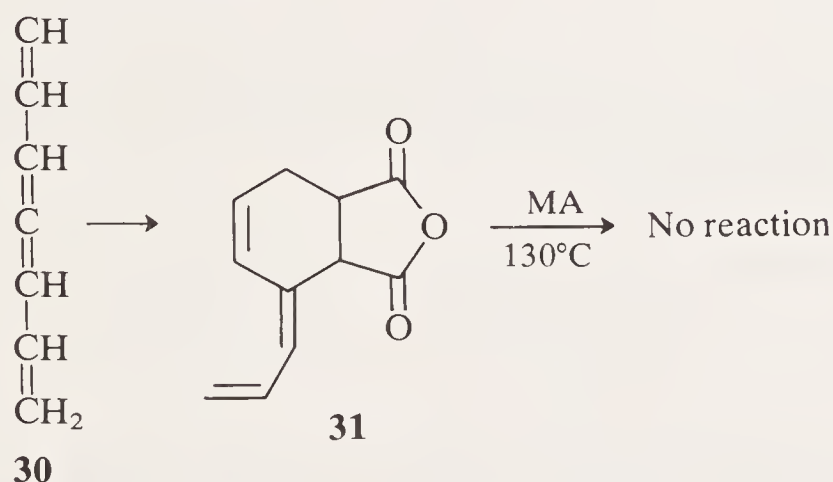
As indicated earlier, one of the diene double bonds can be substituted by a triple bond. The resulting cyclic product then has an additional double bond. When these new bonds are conjugated with other olefinic linkages, a further adduct is formed. Thus, 2,5-dimethyl-1,5-hexadiene-3-yne **23** reacts with 2 moles of MA to give product **24**.<sup>(7)</sup>



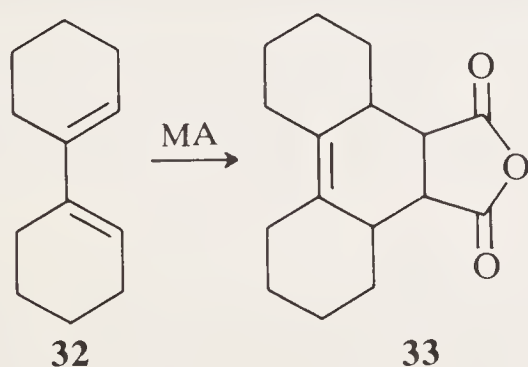
Allene **25** reacts through its dimer **26** as a diene. Alder and Ackerman<sup>(24)</sup> obtained adduct **29**. The proposed route to **29** is shown below:



DA adduct formation by divinylallene **30** with MA has been reported by Modlhammer and Hopf<sup>(25)</sup> to give a monoadduct **31** in a 65% yield. Although the adduct possesses a diene unit, it does not add a second molecule of MA even at 130°C.



It is also possible for the two olefinic units of the diene to be in two different alicyclic rings. As shown below, 1,1'-bicyclohexenyl **32** gives the product with a partially hydrogenated phenanthrene nucleus **33**.<sup>(26)</sup>

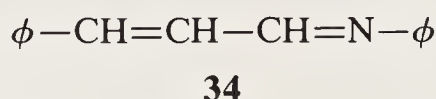


Recently, McMullen *et al.*<sup>(221)</sup> have reported that 1,1'-bicyclobutenyl reacts with MA only in the presence of cupric chloride to give 35–40% of the adduct.

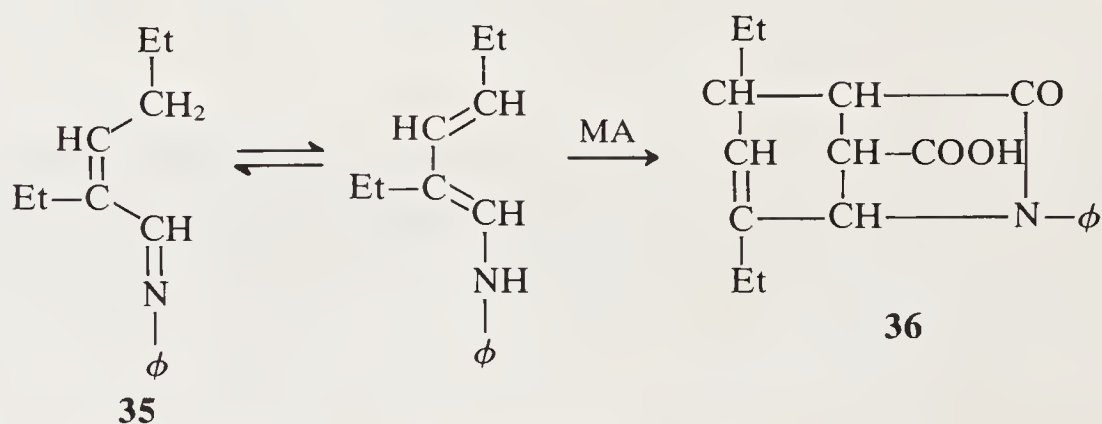


## 4.3.2. Acyclic Dienes with Heteroatoms

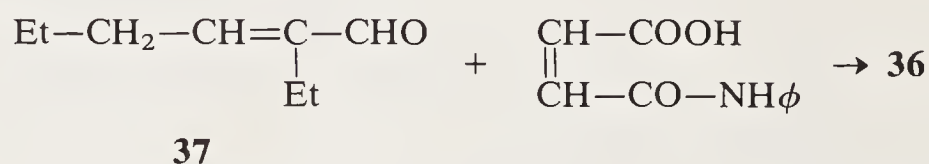
In Eq. (4.2) presented earlier, the atoms a and/or b may be nitrogen as a part of the diene. In such situations, in open-chain dienes, they present interesting cases. For instance, Schiff bases do not react with MA to give DA adducts, e.g., in cinnamal aniline **34**. If any water is present, reactions corresponding to amine and anhydride are evident.<sup>(27,35)</sup> However, in cases where



tautomerism can produce a diene, involving all carbons as shown below, both reactions, i.e., DA and that of amine moiety, occur.<sup>(28)</sup> It has been observed

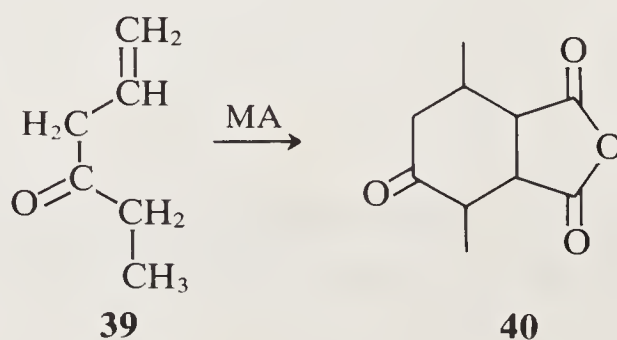


that the same product **36** is obtained by heating 2-ethylhexenal **37** and *N*-phenylmaleiamic acid **38**.<sup>(29)</sup>



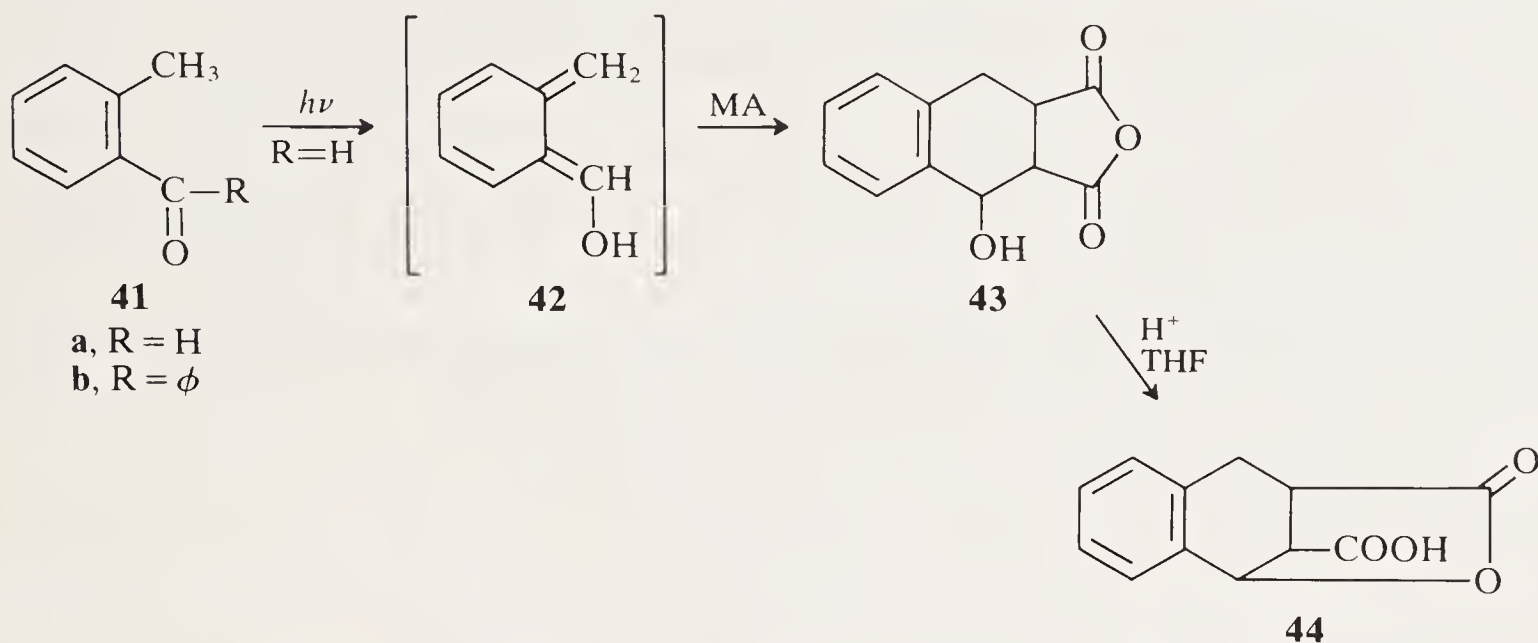
Synthetically the latter may be a more convenient route to **36** since it avoids preparation of anils, and synthesis of maleiamic acids is both easy and gives high yield (see Chapter 3).

The formation of the diene precursor from the anil above requires a tautomerization step. Such additions following tautomerization are not unique as seen in the reaction of crotonaldehyde with naphthoquinone<sup>(30)</sup> and dimerization of crotonaldehyde<sup>(31)</sup> each forming a carbocyclic ring. In such a case, an acid or base catalyst should be present. Berner<sup>(32)</sup> obtained a 40% yield

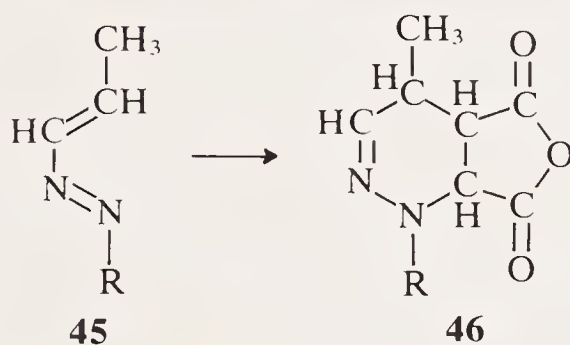


of MA adduct **40** from ethylallylketone **39**, which proceeds via enolization to produce a diene.

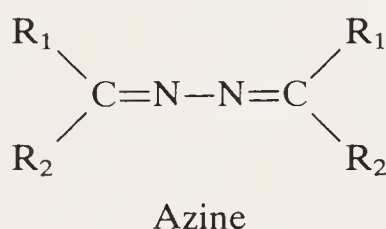
The enolization of some systems such as *o*-tolualdehyde **41a** and *o*-methylbenzophenone **41b** may be initiated by the action of light.<sup>(33,34)</sup> The photo-enols so generated then function as dienes. For example, **41a** reacts through its photoenol **42** to yield the adduct **43**. The latter could be easily converted to the lactone **44** by heating in THF containing sulfuric acid.<sup>(33)</sup>



For compounds in which both a and b atoms are nitrogens as in 1,2-diaza-1,3-butadiene **45**, normal 1,4 addition occurs forming a heterocyclic ring as



in compound **46**.<sup>(36)</sup> Normal adducts are not obtained from azines, where b and c atoms are both nitrogen. (See Chapter 7.)



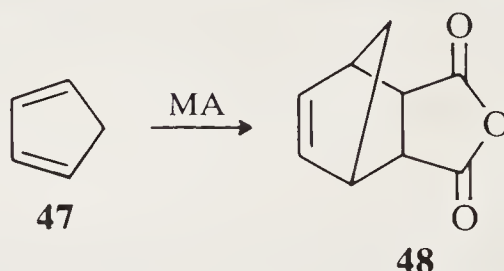
#### 4.3.3. Alicyclic Dienes and the Effect of Ring Size

When the diene unit forms a part of only one ring, as 4-8 member carbocycles, the *cis* configuration is natural. Thus with these dienes, especially when strain does not forbid it, facile reaction may be expected.

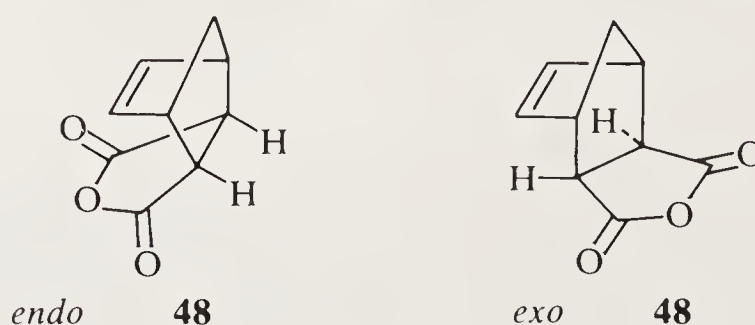
As would be obvious from molecular models, cyclobutadiene would be highly strained and hence very reactive. There is no evidence of MA reacting with cyclobutadiene reported. However, Cava and Mitchell<sup>(37)</sup> have successfully isolated the adduct of benzocyclobutadiene with *N*-phenyl-maleimide, using the latter as a trapping agent. The five- and six-membered dienes can easily achieve the necessary cisoid configuration and hence are very reactive. Cycloheptadiene forms an adduct easily but less readily than cyclopentadiene and cyclohexadiene.<sup>(38-40)</sup> Individual cases are discussed below.

During the diene synthesis, the formation of the six-membered ring gives added thermodynamic stability, particularly for the open-chain dienes. When using cyclic dienes, the stability attained may not be high and an equilibrium may set in. Therefore, as will be seen soon, a number of reactions of cyclic dienes are reversible.

Cyclopentadiene **47** reacts with maleic anhydride at room temperature to give a quantitative yield of the anhydride adduct **48**.<sup>(1)</sup>



Although a detailed account of stereochemistry is deferred until later, this is a good point to digress and talk about the stereochemistry of the isomers produced. In the above-mentioned reactions, two possible isomers may form as shown below:

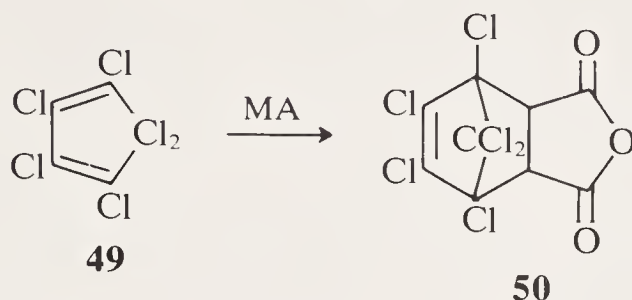


The designation *endo* (inside) means that the substituent (the anhydride ring) is directed to the inside (convex side) of the boat form of the cyclohexane ring. *Exo* (outside) means the substituent is oriented to the concave side (outside) of the boat form of the ring.<sup>(41)</sup> (The ring means the newly formed ring.) In most cases the *endo* product, being kinetically controlled, predominates initially. However, as we shall see later, sometimes only the *exo* product is isolated.

Cyclopentadiene with the diene already in the cisoid configuration reacts very readily with MA to give a quantitative yield of the *endo* adduct.<sup>(42)</sup> A number of cyclopentadiene derivatives have been reacted with MA successfully. Primarily, alkyl and aryl derivatives<sup>(1,42-44)</sup> were investigated. These

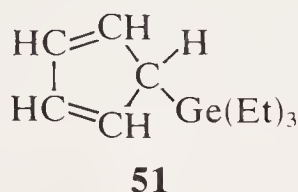


derivatives provide the bicycloheptane structure akin to that in camphor and hence are important synthetically. Hexachlorocyclopentadiene **49** and MA react to form 1,4,5,6,7,7-hexachlorobicyclo-[2,2,1]-5-heptene-2,3-dicarboxylic anhydride **50**.<sup>(45)</sup> Compound **50** is the anhydride of the popular

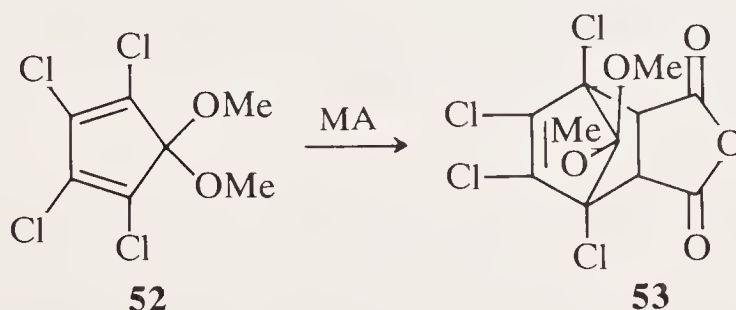


chlorendic acid or Het acid. It contains 54% chlorine by weight and is, therefore, used to impart flame resistance to resins and paints. Hexafluorocyclopentadiene does not react with MA reflecting the high electronegativity of the fluorine atom.

Some cyclopentadienylmetal derivatives also undergo the DA reaction. Mironov *et al.*<sup>(46)</sup> have obtained a 1:1 MA adduct from cyclopentadienyltriethylgermane **51**.

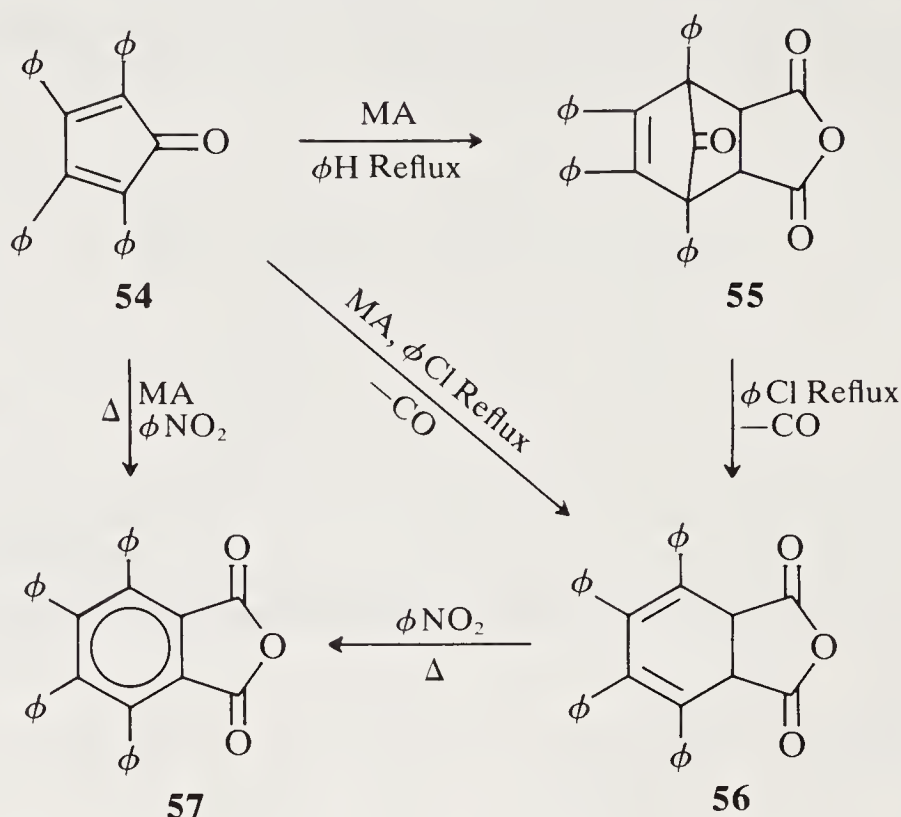


Cyclopentadienone itself occurs as a dimer (produced by DA reaction). No MA adduct using the dimer has been reported. However, for those cyclopentadienone derivatives which occur as monomers or in which adduct formation may compete with dimerization, reactions with MA are observed. For example, the dimethylketal of tetrachlorocyclopentadienone **52** was reported to give near quantitative yield of the adduct **53** on heating at 140°C

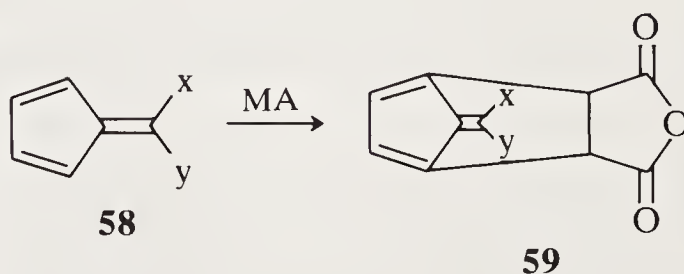


for 2 h with MA.<sup>(47)</sup> Ketals of cyclopentadienone have also been produced by pyrolysis and trapped *in situ* with MA to give the desired adducts.<sup>(48)</sup> Tetraphenylcyclopentadienone **54** (tetracyclone) forms an adduct **55**. The scheme below illustrates some synthetic possibilities exploited in the past.<sup>(23,49,50)</sup> Many cyclones are reactive in the DA reaction with MA and this reactivity has been correlated with their donor–acceptor properties.<sup>(51)</sup>

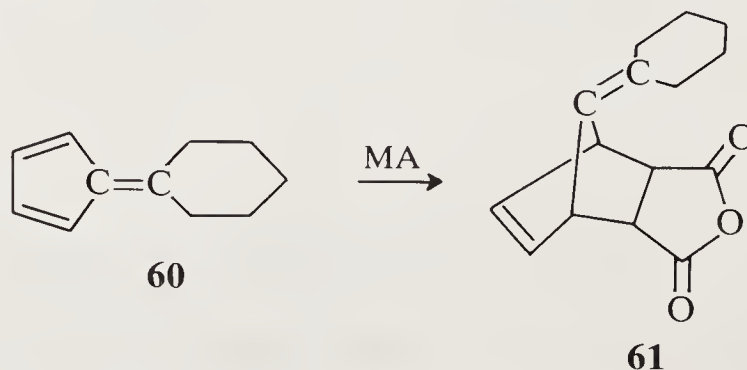
A bisphthalic anhydride monomer has been prepared using a substituted cyclone recently.<sup>(225)</sup>



In fulvenes **58** the exocyclic double bond, although in conjugation with the cyclic diene unit, can not exist in the cisoid diene structure in the ring. Hence in all cases known, fulvenes form adducts utilizing the cisoid diene in the ring, giving **59**.<sup>(52-56)</sup>



It was recognized quite early by Alder and Ruhrman<sup>(58)</sup> that the reaction of pentamethylenefulvene **60** gave a mixture of adducts, i.e., 40% *endo* and 60% *exo*. Woodward and Baer<sup>(57)</sup> have shown that the *endo* isomer of **61**



dissociates into its components in solution even at room temperature and equilibrates to obtain the thermodynamically more stable *exo* adduct. Similar

Table 4.2. Temperature Dependence of *exo:endo* Product Distribution from Dimethylfulvene (5 g) and MA (5 g)<sup>a</sup>

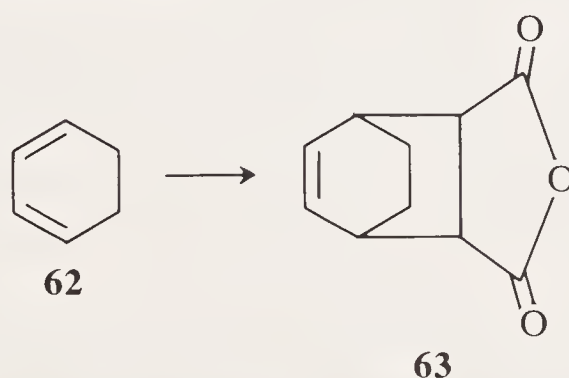
Condition	Isomers (g)	
	<i>exo</i>	<i>endo</i>
0°C	2.6	3.4
38°C (in ether)	3.3	2.6
80°C (reflux benzene)	6.2	0.7

<sup>a</sup> From Reference 58.

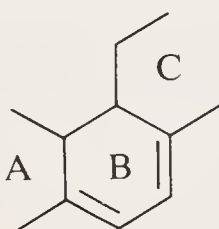
temperature dependence of the steric outcome of the reaction of dimethylfulvene **58** ( $x = y = \text{CH}_3$ ) with MA was demonstrated by Alder and Ruhrmann<sup>(58)</sup> and are shown in Table 4.2.

Craig *et al.*<sup>(59)</sup> have also shown that dimethylfulvene **58** ( $x = y = \text{CH}_3$ ) formed predominantly *exo* isomers at higher temperatures. Interestingly, they showed that both *endo* and *exo* isomers undergo retroreactions to give the starting material, the former faster than the latter. Retroreaction was shown to be unnecessary for the isomerization of the product because the presence of MA did not alter the rate of isomerization although the rate of dissociation was reduced.

The reaction of dienes in a six-membered ring has been studied a great deal. By the reaction of 1,3-cyclohexadiene **62** one obtains a bicyclooctene derivative **63** in quantitative yield.<sup>(1,60)</sup>



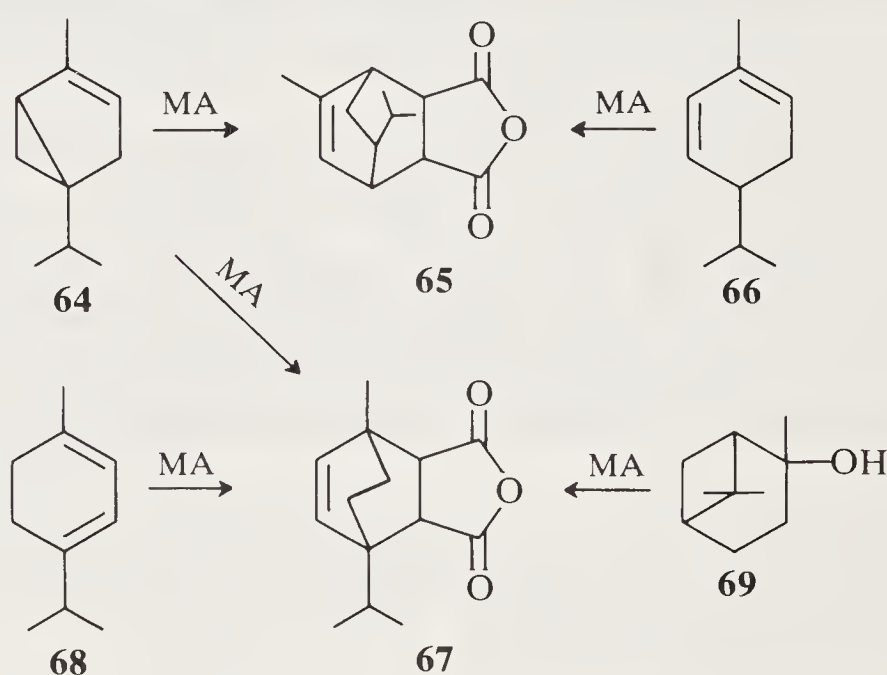
Since a number of natural products have cyclohexadiene structure, adduct formation has been used in the past as a means of identifying cisoid diene configuration for the structure determination of the natural products. For example, ergosterol series isomers, namely, lumisterol, pyrocalciferol, and isopyrocalciferol, possess a 1,3-diene system in the B ring. Each of these





isomers react with maleic anhydride to form the corresponding adduct. This is also an interesting proof that the steric arrangement at other positions have little influence on the Diels–Alder reaction.<sup>(61)</sup>

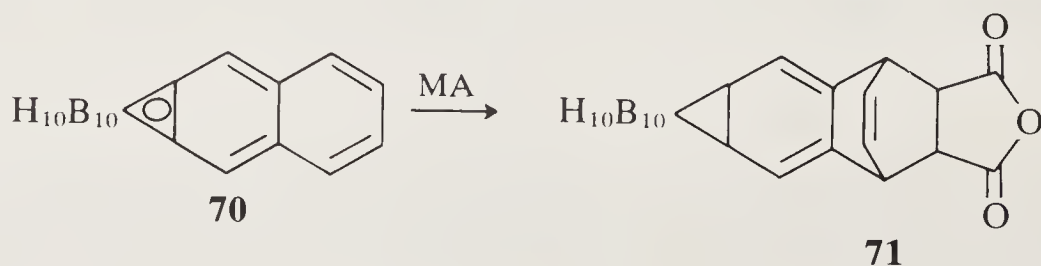
The chemistry of natural products such as terpenes also shows an interesting feature, i.e., the diene can form *in situ* by rearrangement such as cleavage of a cyclopropane or cyclobutane ring. Thus, thujene **64** reacts with maleic anhydride to give two adducts.<sup>(62)</sup> The adduct **65** is identical with that obtained from  $\alpha$ -phellandrene **66**. The other adduct **67** is the same as the one obtained from  $\alpha$ -terpinene **68**. The adduct **67** is also obtained from 4-methyl-4-nopinol **69**,<sup>(63)</sup> a terpene alcohol that gives rise to the elements of the diene by dehydration and rearrangement of the cyclobutane ring. These interesting transformations have played a very important role in proving structures of these natural products. The scheme below illustrates these relationships.<sup>(23)</sup>



A number of terpenes, such as  $\alpha$ -pinene and terpinolene, react with maleic acid to yield an adduct obtained from  $\alpha$ -terpinene. With maleic anhydride, on the other hand, a product corresponding to an ene reaction is obtained. Acid apparently catalyses the rearrangement of these terpenes to  $\alpha$ -terpinene prior to addition.<sup>(23)</sup>

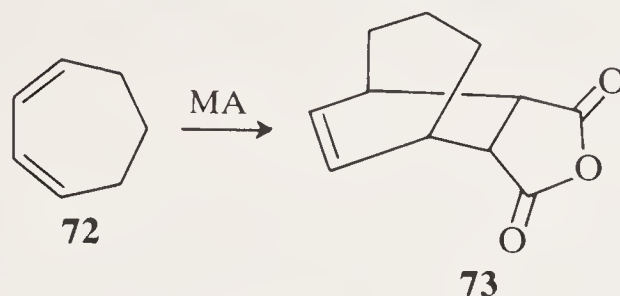
It would be difficult to leave this topic without saying that the Diels–Alder reaction has played a very important role in the structure proof of the terpenes by virtue of their synthesis. Interested readers are referred to excellent reviews and original literature.<sup>(23,61)</sup>

An unusual cyclohexadiene system has been recently reported by Matteson and Davis.<sup>(64)</sup> They observed that naphthocarborane **70** yields the adduct

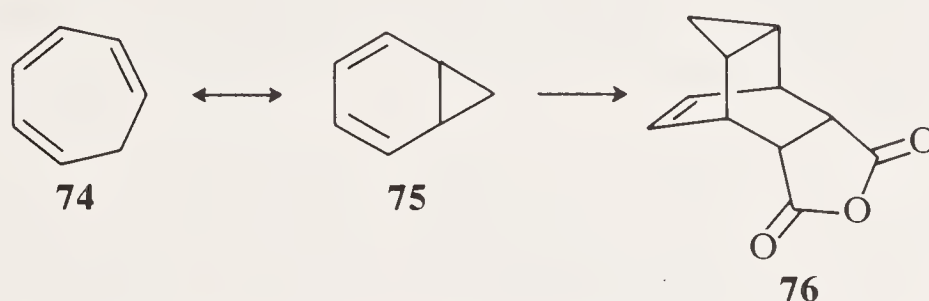


**71** in an 88% yield when heated at 100°C for 8 h. The structure assignment was done by NMR.

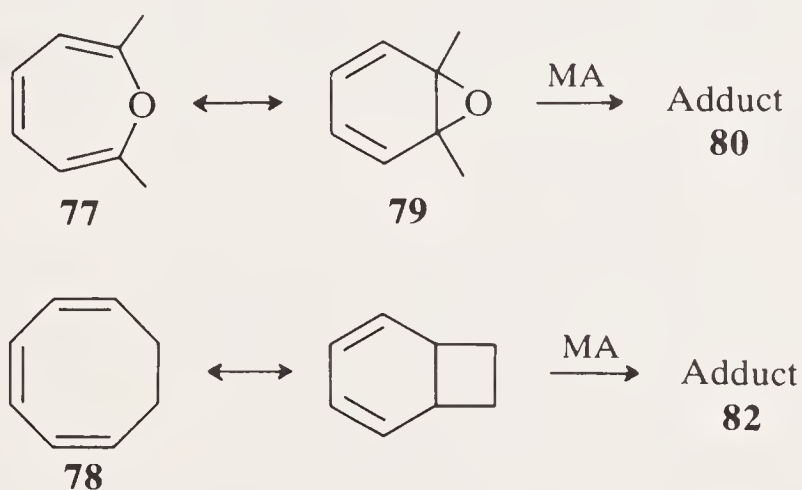
Cycloheptadiene **72** gives a high yield of the adduct **73** in refluxing xylene. The *endo* structure was assigned to product **73** by Alder and Molls.<sup>(65)</sup>



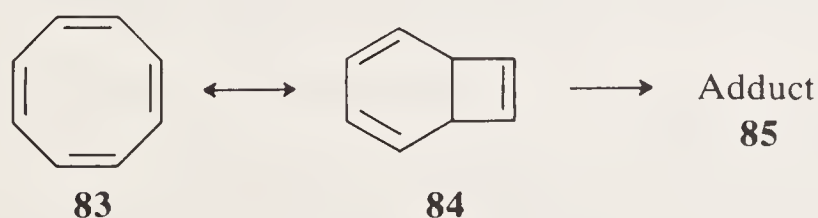
Cycloheptatriene **74**, on the other hand, reacts through its valence bond tautomer, bicycloheptadiene **75**, to yield the bridged adduct **76** as the main product.<sup>(66–68)</sup> A product corresponding to direct addition to **74** was also observed.<sup>(68)</sup> A number of tropilidene derivatives (i.e., cycloheptatriene derivatives)<sup>(69)</sup> and tropolones<sup>(70,71)</sup> have also been reported.



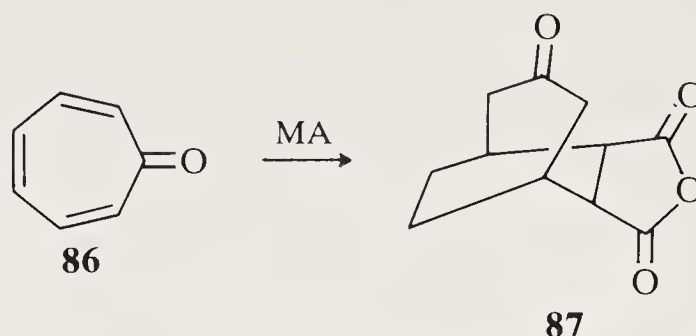
A valence-bond tautomerism is also evident in other systems such as the oxepin derivative **77**<sup>(72,73)</sup> and cyclooctatriene **78**<sup>(74)</sup> as shown below:



Cyclooctatetraene **83** has also been shown to yield an addition product of the diene formed from the valence bond tautomerization.<sup>(75)</sup> However,



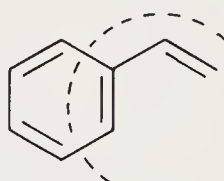
tropone **86** adds maleic anhydride while retaining the seven-membered ring.<sup>(76)</sup>



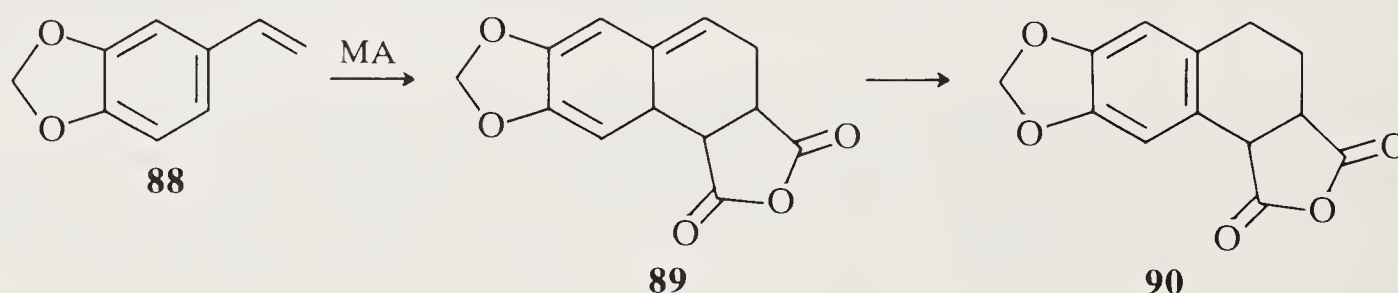
Medium-sized carbocyclic dienes containing 8–11 carbon atoms do not form adducts with MA<sup>(77,78)</sup> because attainment of a planar cisoid configuration is practically impossible. However, as ring size is enlarged to 12, 13, and higher, the strain is reduced allowing a planar cisoid conformation. As a result these 1,3 dienes do form maleic anhydride adducts in low yield.<sup>(79,80)</sup>

#### 4.3.4. Part of the Diene in the Aromatic Ring (Styrene Derivatives)

A substituted styrene may be viewed as containing a diene as illustrated below. The exocyclic double bond with the aromatic nucleus may form a reactive diene unit.



This requires disruption of the aromatic conjugation and hence the resonance stability—at least in the transition state. (The aromaticity may be regenerated in the product.) Reactions where such participation are evident are known, e.g., the reaction of isosafrole **88** with MA illustrated below.<sup>(81,82)</sup> It is believed that the initially formed adduct **89** rapidly rearranges to the aromatic product **90**.

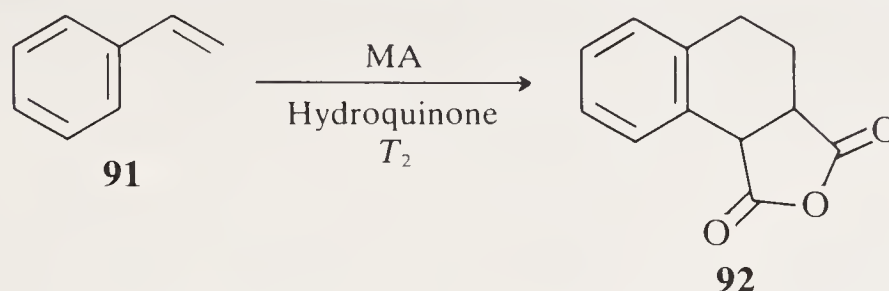


Hudson and Robinson<sup>(81)</sup> studied a series of substituted styrenes with maleic anhydride. They reported unsubstituted styrene **91** to rapidly polymerize with MA. Some of their observations were as follows:

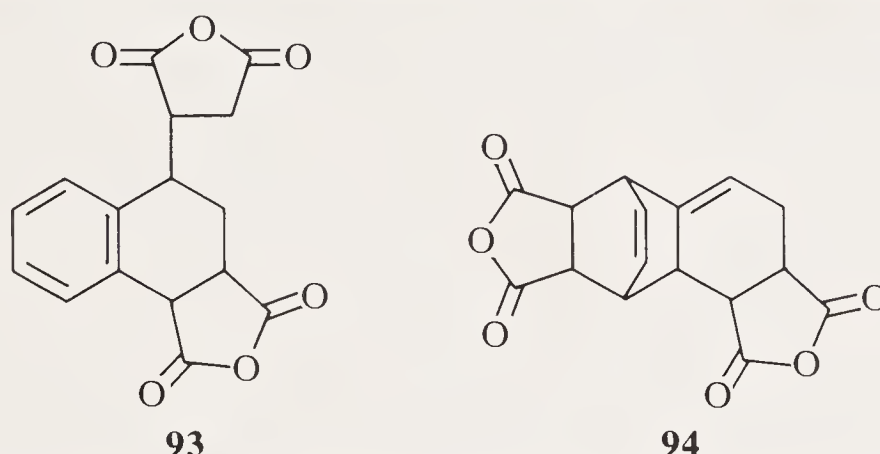
- (i) The alkoxy group in the *para* position enhances the tendency to DA reaction with MA.
- (ii) The *meta* alkoxy group has no such effect.
- (iii) The  $\beta$ -alkyl substitution in styrene generally gives the DA adduct.



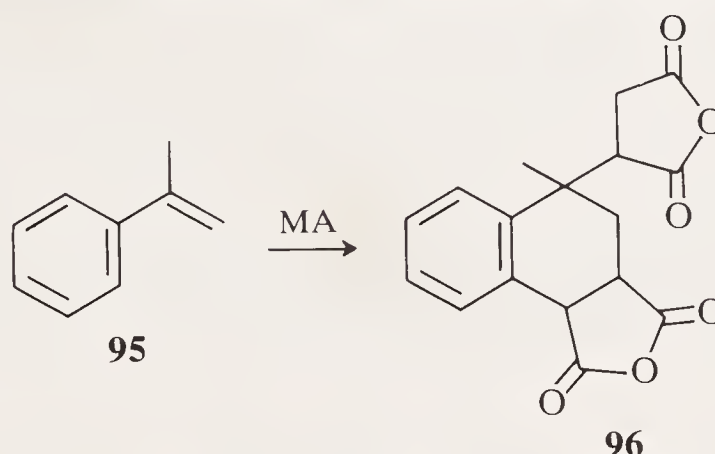
Later, Alder and coworkers reported the synthesis of an acid derivative of the monoadduct **92** from styrene **91** and MA.<sup>(83)</sup> In the presence of picric



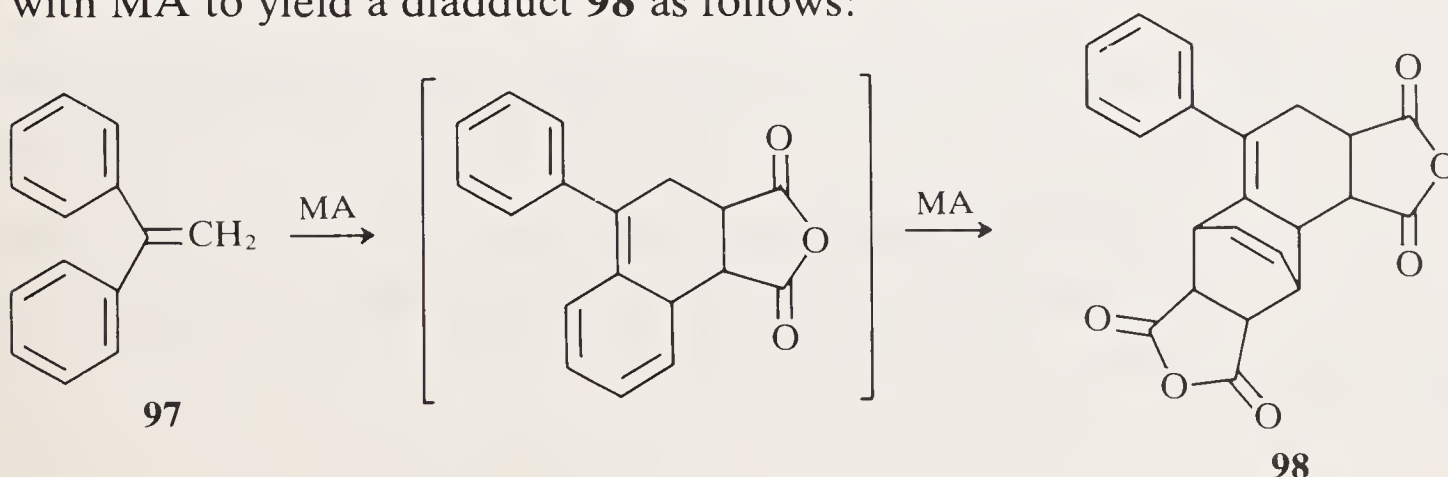
acid in refluxing benzene, however, they isolated the diadducts **93** and **94**. Note that **93** arises from the ene reaction of the intermediate structure



analogous to structure **89**, whereas the DA addition on the diene segment leads to **94**. Zadra and Tazuma<sup>(84)</sup> have recently patented a detergent based on the diadduct **96** made from  $\alpha$ -methylstyrene **95** and MA.

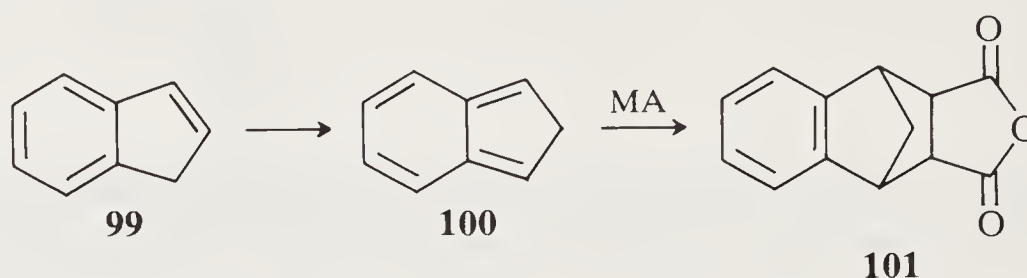


It is probably evident that since disruption of aromaticity is required, the reaction conditions required for these systems are more drastic than simple dienes. This allows further reactions. Thus, 1,1-diphenylethylene **97** reacts with MA to yield a diadduct **98** as follows:



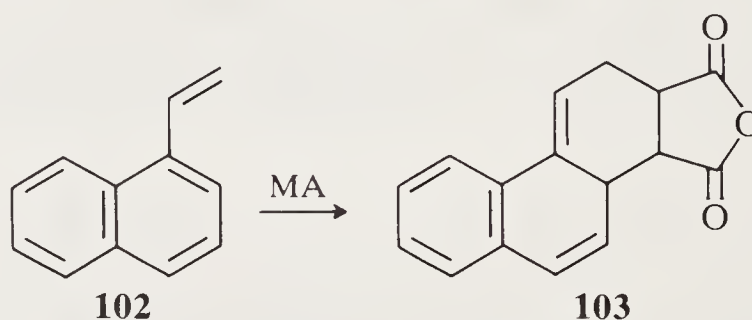
The formation of the diadduct suggests that the aromatization of the intermediate is at least competitive with the addition of the second mole of MA.<sup>(85,95,96)</sup>

Indene (benzocyclopentadiene) **99** also reacts with MA. In this case, a 1,4 addition requires rearrangement to isoindene **100** and hence loss of aromaticity during the reaction occurs as shown below:<sup>(86)</sup>

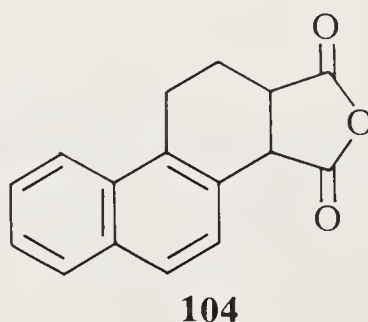


That such a rearrangement does occur under the condition of the DA reaction has been shown by Roth<sup>(87)</sup> and Isaacs.<sup>(88)</sup> Similar conclusions were also arrived at by Berson.<sup>(89)</sup> Note that **100** has two diene units—namely, cyclopentadiene and cyclohexadiene. Only the former is reported to react with MA. This is not necessarily true of other dienophiles.<sup>(228)</sup>

Exocyclic conjugation in the naphthalene or phenanthrene nucleus often yields a diene reaction with maleic anhydride as illustrated below with 1-vinylnaphthalene **102**.<sup>(90-93)</sup> In refluxing toluene or xylene **103** can be isolated.

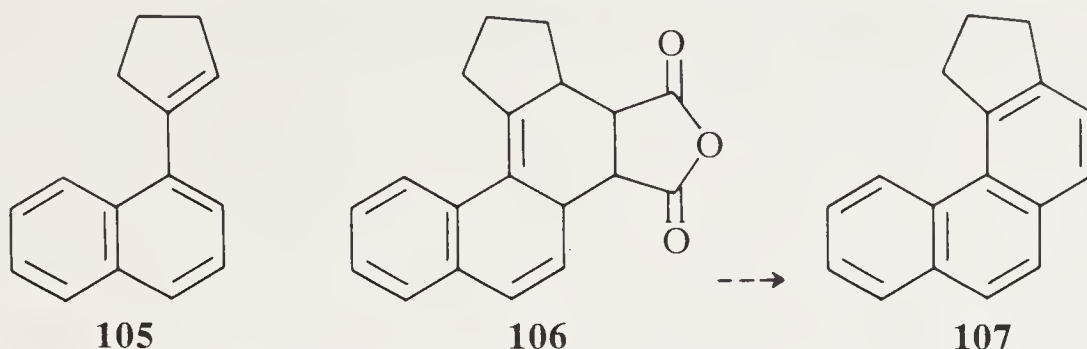


However, in acetic acid the aromatized product **104** is obtained. Adduct **103** can also be converted to **104** by refluxing the acetic acid/HCl solvent. An



interesting observation made was that the reaction with a *trans*-dienophile, e.g., fumaric acid, gave a cleaner reaction mixture than the *cis*-dienophile (MA) since less polymeric material was produced.<sup>(92,93)</sup> The above reactions yield polycyclic products (phenanthrene derivatives), which are important building blocks for steroids, alkaloids, and polycyclic aromatic compounds. Many related systems have recently appeared in an excellent review by Wagner-Jauregg.<sup>(227)</sup>

The exocyclic olefin can itself be a part of the ring as shown by the synthesis of a phenanthrene derivative **107** from 1-naphthyl-1-cyclopentene **105**.<sup>(94)</sup> The adduct **106** can be converted to the aromatic hydrocarbon **107**.

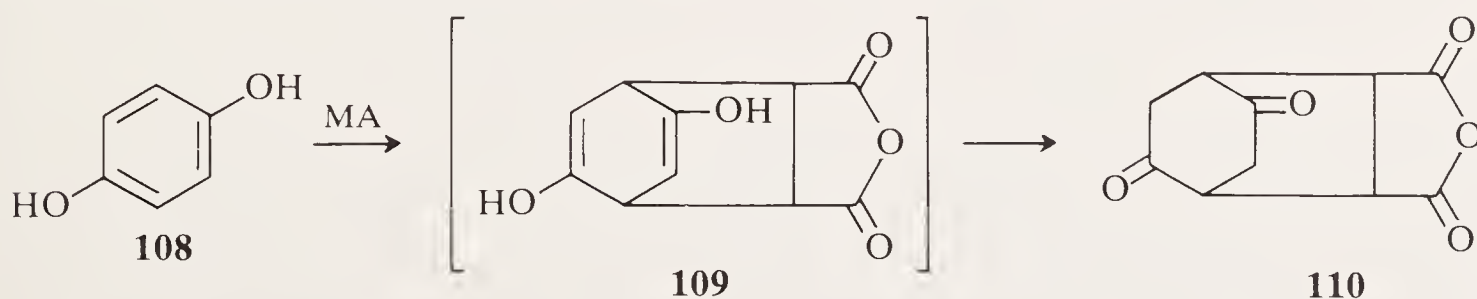


Similarly, the  $\beta$ -cyclopentene derivative of naphthalene also gives an excellent yield of the adduct as well as the corresponding aromatic hydrocarbon.<sup>(94)</sup>

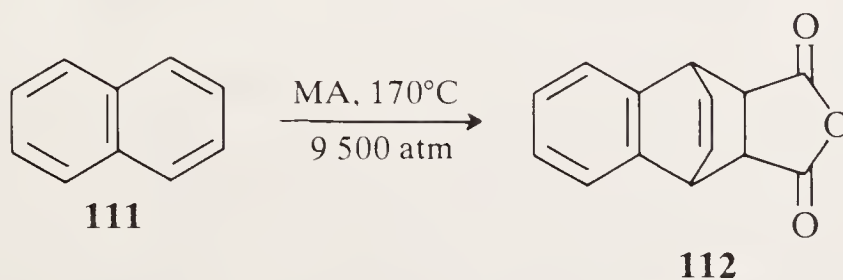
#### 4.3.5. Aromatic Compounds

When an aromatic compound adds MA, generally, the resonance stabilization of such a system is destroyed. When loss of resonance energies are significant, high activation energies are anticipated for these reactions. Thus, simple aromatic compounds tend to be less reactive as dienes. In the series benzene, naphthalene, and anthracene, examination of canonical structure suggests that the middle ring of anthracene has the most dienelike character. The normal order of reactivity observed, therefore, is benzene < naphthalene < anthracene.

Benzene reacts very sluggishly, and no 1:1 adduct with MA has been isolated.<sup>(78)</sup> However, the benzene ring in cyclophanes may be sufficiently strained to be more trienic than aromatic. A 1:1 DA adduct of MA with a cyclophane has been reported.<sup>(222)</sup> Hydroquinone **108** also is sufficiently activated to produce low yields of the adduct **110**.<sup>(97,98)</sup> Note that product **110** is the ketonic form of the initially produced adduct **109**.



Under ordinary conditions, naphthalene **111** gives very low yields of a mixture of isomeric anhydrides **112**.<sup>(99)</sup> Under forcing conditions, e.g., by

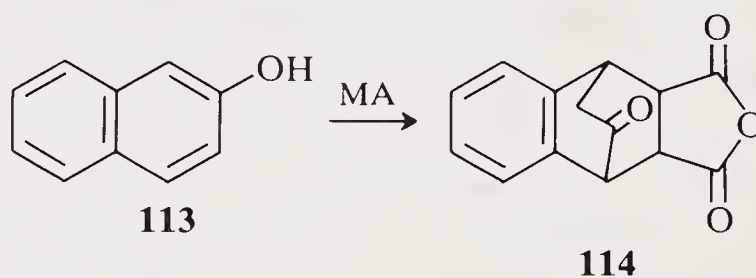




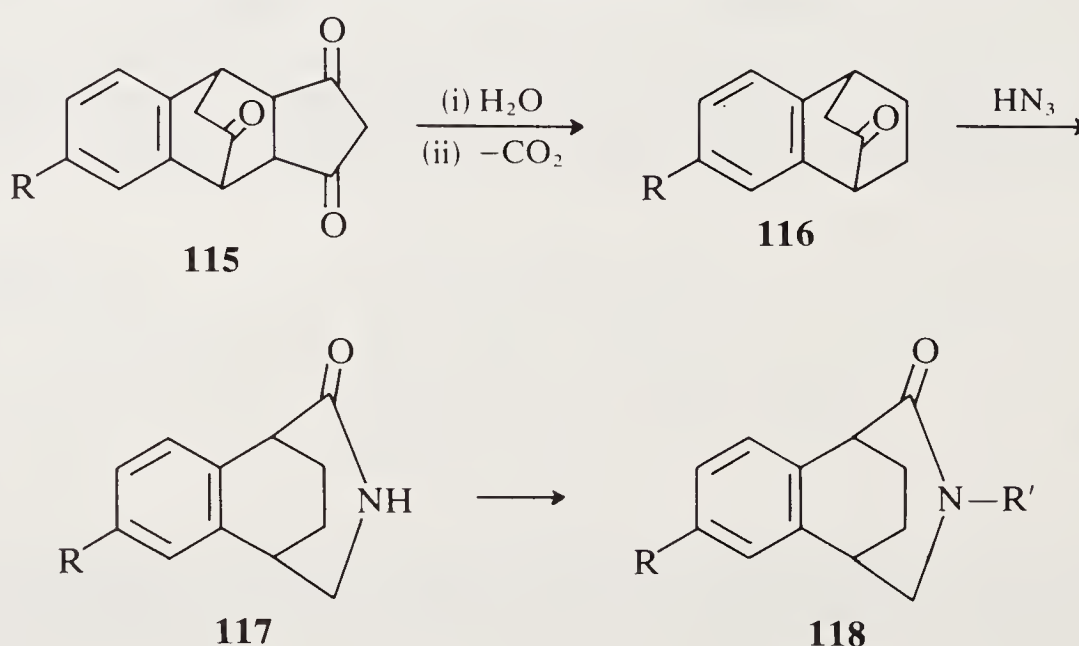
application of 9500 atm of pressure, much improved yields (78%) are obtained.<sup>(100)</sup> Alkyl substitution on the ring favors additions to the substituted ring as observed with 2,3-dimethylnaphthalene and 1,2,3,4-tetramethylnaphthalene.<sup>(101)</sup> The reactants and products are in equilibrium and hence, using a large excess of maleic anhydride, very high yields of the adduct can be obtained.<sup>(101,102)</sup> From the relative mildness of conditions used by Kloetzel and Herzog<sup>(101)</sup> compared to that needed for naphthalene **111**, it appears that methyl substitution increases the diene reactivity of naphthalene. Oku *et al.*<sup>(103)</sup> have studied the relative rates of polymethylnaphthalenes. All the adducts were produced in high yields. Kinetically, the *endo*-isomer is preferred whereas the *exo*-isomer is thermodynamically more stable. The reactivities of various polymethylnaphthalenes are compared in Table 4.3.

Nitro substitution, as in 1-nitronaphthalene, makes forcing conditions necessary, and addition takes place in the unsubstituted ring across the 5,8 positions.<sup>(100)</sup>

The ring in 2-naphthol **113** is sufficiently activated to act as a diene. On reaction with MA two stereoisomers of adduct **114** are formed, which is the



keto form.<sup>(103–105)</sup> This chemistry is utilized in an interesting way by Danayer<sup>(106)</sup> in the design of synthetic drugs as illustrated below:



Coating compositions containing **114** have also been proposed.<sup>(107)</sup>

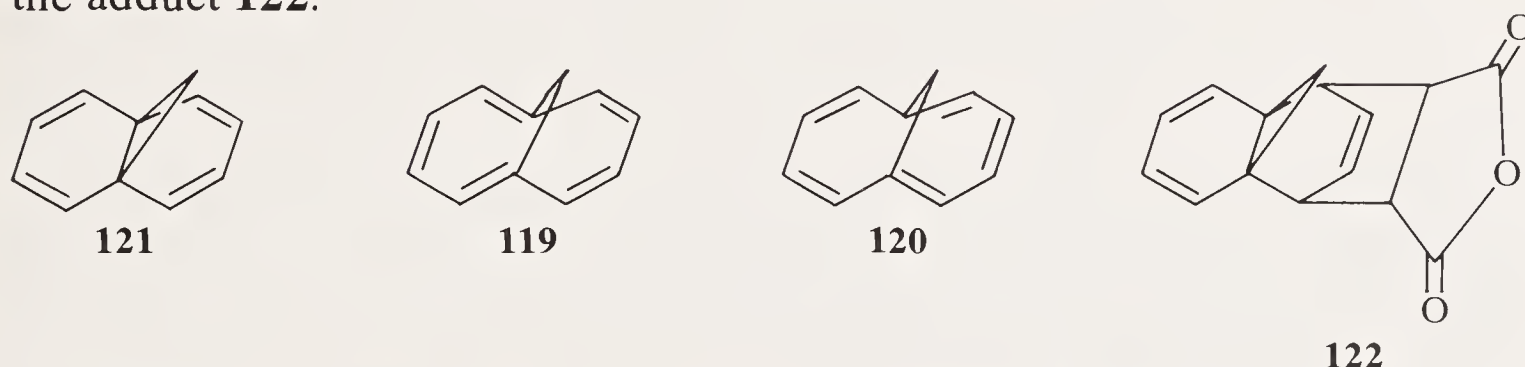
It is of interest at this point to mention another  $[4n + 2]$  aromatic hydrocarbon, namely, 1,6-methenocyclodecapentaene **119**, synthesized by Vogel and coworkers.<sup>(78,108)</sup> Like naphthalene, it has a cyclic conjugated  $10\pi$  electron system and hence aromatic character is expected. It does react with

Table 4.3. Relative Rates of DA Reaction of Polymethylnaphthalenes with MA at 60°C in  $\text{HCCl}_3$ <sup>a</sup>

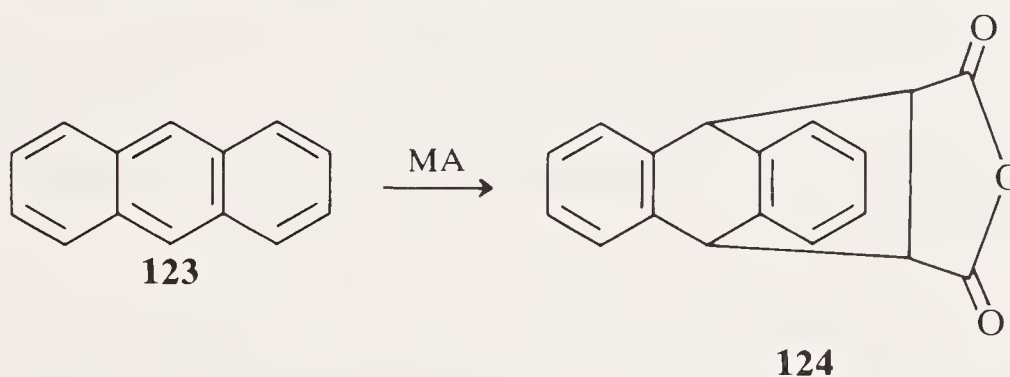
Polymethylnaphthalene	Relative rate
1,2,3,4,5,8-Hexamethyl	4.00
1,2,3,4,5,6,7,8-Octamethyl	1.00
1,2,3,4,6,7-Hexamethyl	0.28
1,2,3,4-Tetramethyl	0.11
1,2,5,6-Tetramethyl	0.03

<sup>a</sup> Reprinted with permission from *J. Org. Chem.* **37**, 4264 (1972). Copyright 1972, American Chemical Society.

1 mole of MA at 150°C, presumably through the valence tautomer **121**, giving the adduct **122**.



Anthracene **123** is very reactive toward maleic anhydride and gives a quantitative yield of the adduct **124** when refluxed in benzene<sup>(1)</sup> for 10 min.



As would be expected, substituted anthracenes differ markedly in their reactivity. Thus, 9-methylantracene and 9,10-dimethylantracene react faster than anthracene itself as was shown by Bachmann and Kloetzel.<sup>(109)</sup> A phenyl group in the *meso* position reduces the reactivity such that 9,10-diphenylantracene **125** adds MA across the 1,4 position as shown below:<sup>(110)</sup>

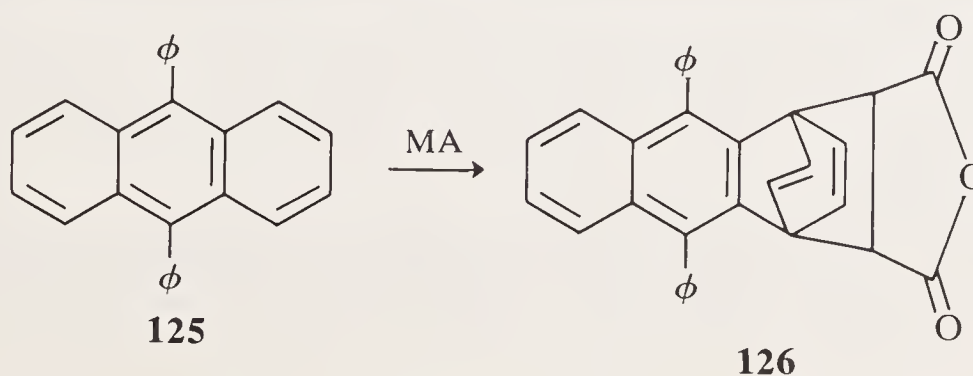


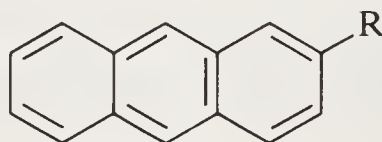
Table 4.4. Dissociation of Anthracene-Maleic Anhydride Adducts<sup>a</sup>

Arene	% Adduct at equilibrium in boiling xylene	
	1 mol Maleic anhydride	30 mol Maleic anhydride
Anthracene	99	—
9-Methylanthracene	99	—
9,10-Dimethylanthracene	98	—
9-Phenylanthracene	75	97
9,10-Diphenylanthracene	16	78
1,2-Benzanthracene	84	99
1,2-5,6-Dibenzanthracene	30	91

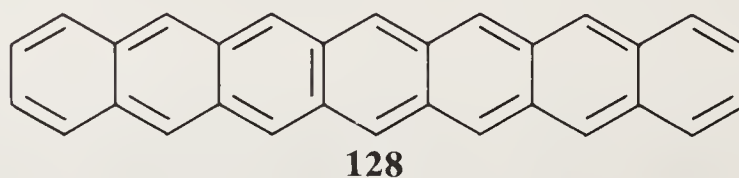
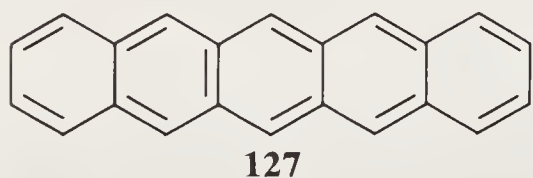
<sup>a</sup> From References 8 and 109.

Since the adduct of anthracene derivatives is in equilibrium with the reactants, many times it is advantageous to use a large excess of MA to obtain preparative amounts of the product. The equilibrium adduct formation and the effect of excess MA in the anthracene series is shown in Table 4.4.<sup>(109)</sup>

Kaplan and Conroy<sup>(111)</sup> have studied a number of 2-substituted anthracenes. It was shown that the reaction rate, as expected, was enhanced with  $R = N(CH_3)_2$  and decreased with  $R = NO_2$ .



When a polycyclic molecule contains (what may appear to be) more than one anthracene unit such as pentacene **127** or heptacene **128**, the addition reaction is facilitated.<sup>(23,112)</sup>

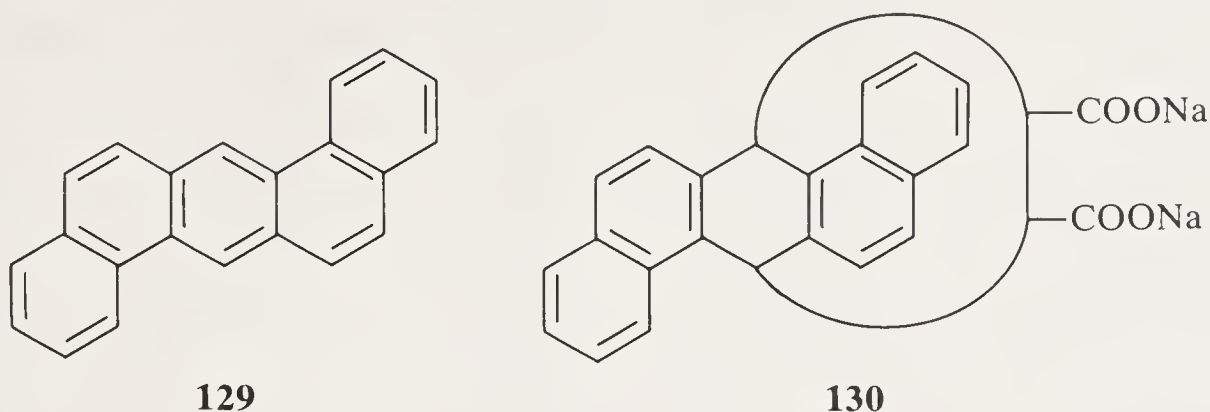


The facility of MA addition to the anthracene system in a polycyclic aromatic was ingeniously utilized in the conversion of a carcinogenic hydrocarbon. For developing anticancer drugs it was necessary to induce cancer rapidly in experimental animals. To this end MA was added to 1,2,5,6-dibenzanthracene **129** and then the resulting anhydride was converted to the water-soluble alkali metal salt **130**.<sup>(113)</sup> These and other salts could then be injected subcutaneously to induce cancer.<sup>(114)</sup>

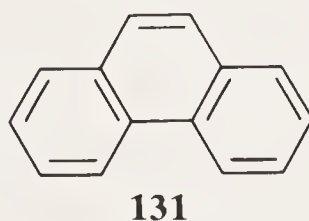
Jones *et al.*<sup>(115)</sup> have utilized MA reactivity with some polynuclear hydrocarbon for separation purposes. Thus, reactive anthracene containing



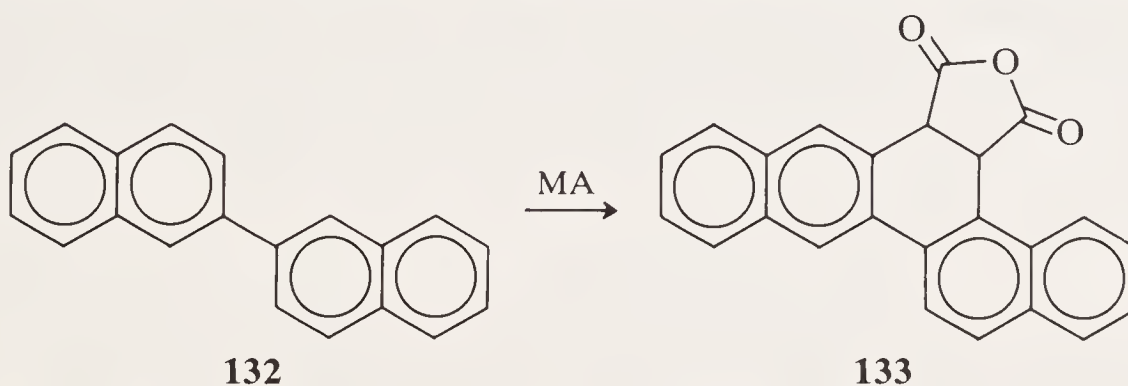
molecules are reacted with MA. Separation of unreacted material is followed by decomposition of the MA adducts into constituents.



In contrast to anthracene, phenanthrene **131** fails to react with MA under the thermal conditions. Photochemical reaction of **131** with MA is known (see Chapter 6).



Among other polycyclic hydrocarbons, apparently diphenyl does not enter into the reaction. A benzo analog of diphenyl, namely, 2,2'-binaphthyl **132** reacts with MA in the presence of iodine to give anhydride **133** as the main product in a complex mixture.<sup>(116)</sup> Note that the diene unit is generated by participation of two aromatic rings. The fate of the ring hydrogen was not clear.



Two aromatic rings are known to participate in other systems as well. Perylene **134**, for example, adds 1 mole of MA in refluxing nitrobenzene. The latter also acts as an oxidizing agent to aromatize the initially formed adduct **135** to the product **136**.<sup>(220)</sup>

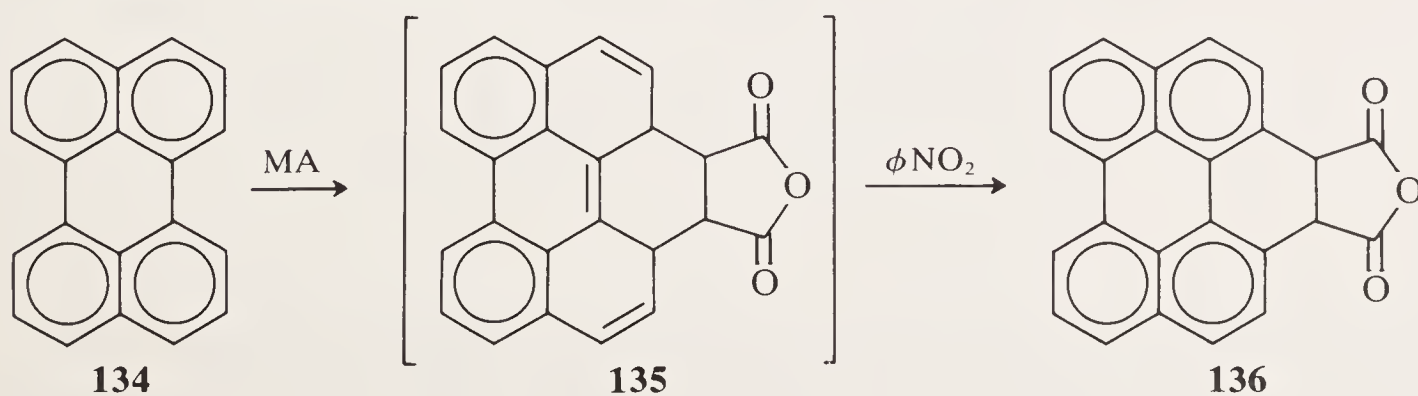


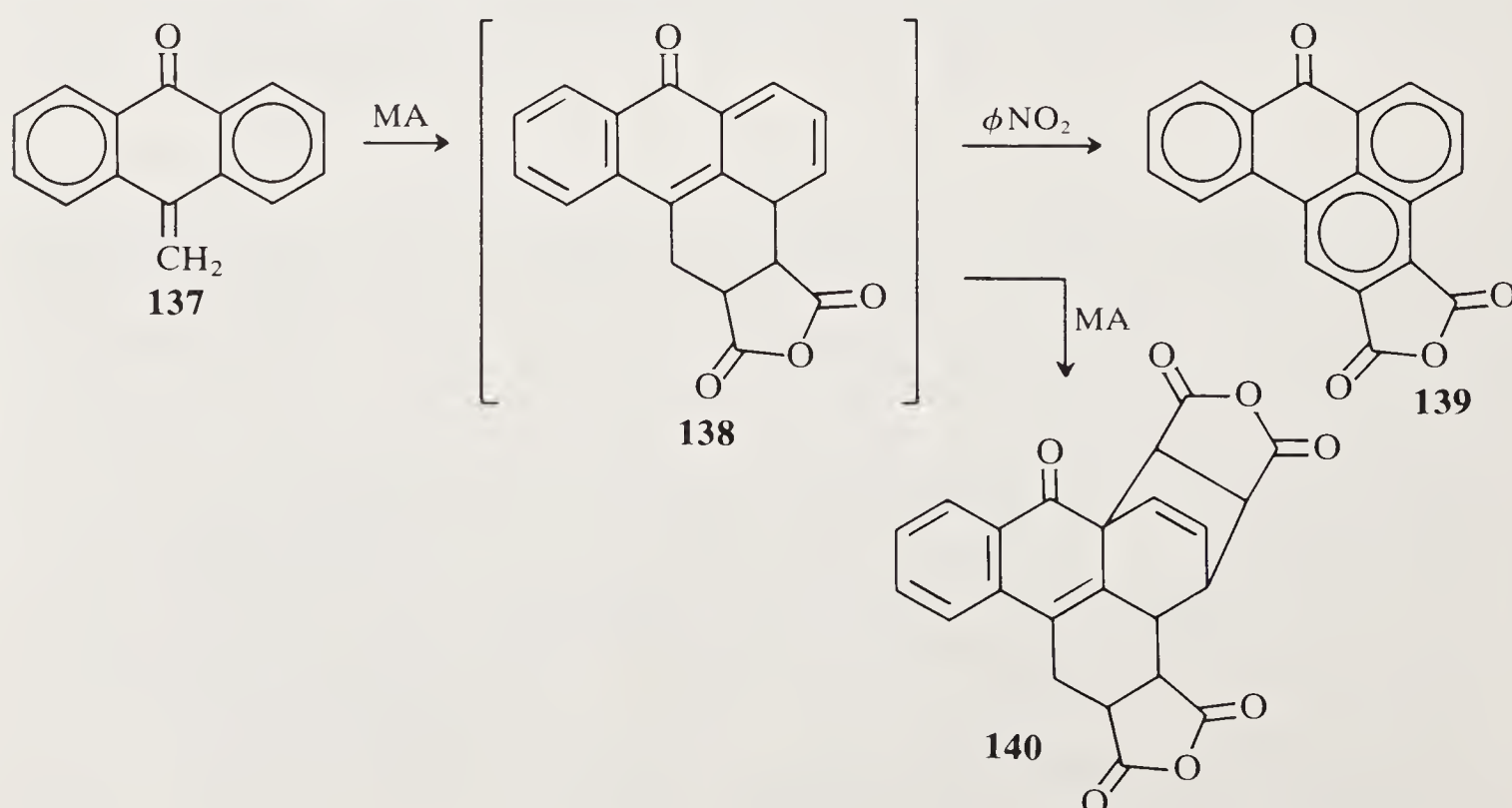
Table 4.5. Diels–Alder Reactions of Aromatic Compounds with Maleic Anhydride<sup>a</sup>

Reactant	Rate constant (1 mol <sup>-1</sup> s <sup>-1</sup> )	Temperature (°C)	$\Delta G^*$ (kcal/mol)	$\Delta RE$ (kcal/mol)
Naphthalene	$1.03 \times 10^{-4}$	155.7	33.2	-9.9
Dibenz[a,j]anthracene	$6.75 \times 10^{-5}$	129.7	31.5	-6.2
Dibenz[a,c]anthracene	$3.58 \times 10^{-4}$	129.7	30.2	-6.7
Benz[a]anthracene	$6.92 \times 10^{-4}$	129.7	29.7	-2.8
Dibenz[a,c]naphthacene	$1.75 \times 10^{-2}$	120.1	28.2	-0.2
Anthracene	$7.55 \times 10^{-3}$	129.7	27.7	+1.9
Benz[a]naphthacene	$4.98 \times 10^{-3}$	70.0	23.8	+7.0
Naphthacene	$2.08 \times 10^{-3}$	39.7	22.2	+10.2
Benz[a]pentacene	$4.31 \times 10^{-3}$	0.0	18.9	+15.3
Pentacene	$5.86 \times 10^{-3}$	0.0	18.7	+16.5

<sup>a</sup> From Reference 117.

A number of perylene derivatives undergo cyclo addition reaction. Hernon<sup>(117)</sup> has shown that the free energies of activation of the reaction of MA with aromatic hydrocarbon has a linear relationship with calculated resonance energy differences. This approach has significant prediction value (see Table 4.5). Recently, kinetic studies of the DA reaction of maleic anhydride with polycyclic aromatics have been reported.<sup>(233–235)</sup>

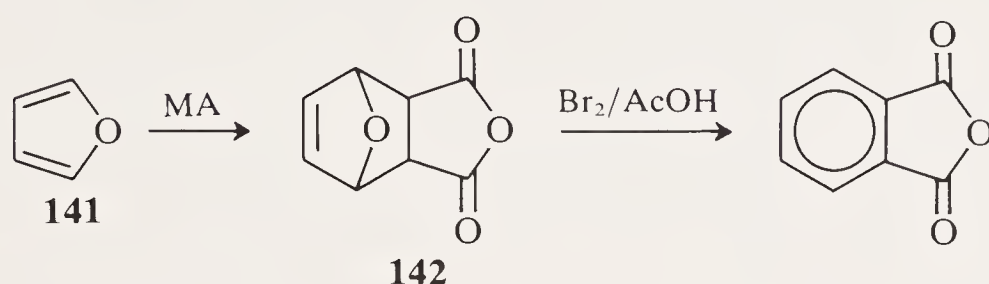
An interesting case of DA reactivity of methylene-anthrone **137** deserves comment.<sup>(82)</sup> The latter reacts with 1 mole of MA in refluxing nitrobenzene to give the adduct **139**. On the other hand, if the reaction is carried out in refluxing acetic acid, 2 moles of MA are added to give **140**. It is evident therefore that the first addition produces a new diene **138** which meets different fates depending on the conditions.



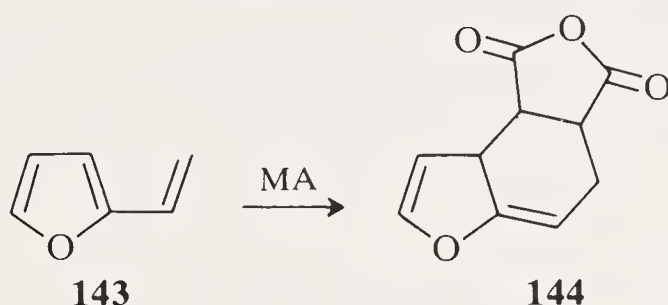
## 4.3.6. Heterocyclic Compounds

## 4.3.6.1. Five-Membered Heterocycles

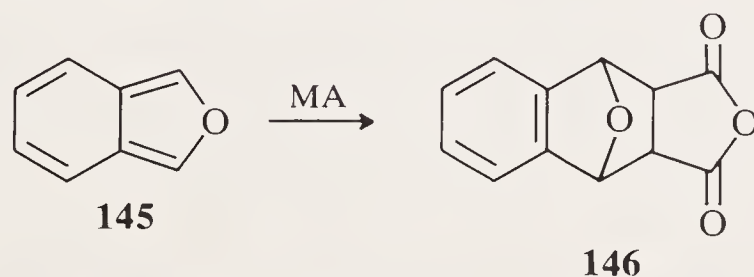
Each of the simple five-membered heterocycles—furan, pyrrole, and thiophene—can be regarded as dienes with varying degrees of aromaticity. They have the  $(4n + 2)\pi$  electronic systems where two of the necessary six electrons are supplied by the heteroatom. Of these, furan appears the least aromatic and hence most dienelike. Furan **141** alone reacts with maleic anhydride under ordinary conditions to form an adduct **142**. The reaction occurs under mild conditions to give quantitative yields.<sup>(118,119,130)</sup> The structure of the adduct **142** has been verified by converting it to phthalic anhydride.<sup>(130)</sup>



A number of furan derivatives, e.g., 2-methylfuran, 3-methylfuran, 2,5-dimethylfuran, 3-bromofuran, and 2-aminofuran, have been investigated.<sup>(23,120,147,231)</sup> Furan derivatives with 2 or 3 cyano, carbethoxy, and nitro substituents fail to undergo the addition reaction. However, when a double bond is exocyclic to a furan ring, interestingly, the adduct formed is predominantly the one involving the external olefin as known in the case of 2-vinylfuran **143**.<sup>(121,122)</sup> Numerous isobenzofuran **145** derivatives have



been examined and reportedly give the expected adduct **146** in good yields under relatively mild conditions.<sup>(123–129,223)</sup> This may be due to the aromatization brought about as a consequence of the reaction.



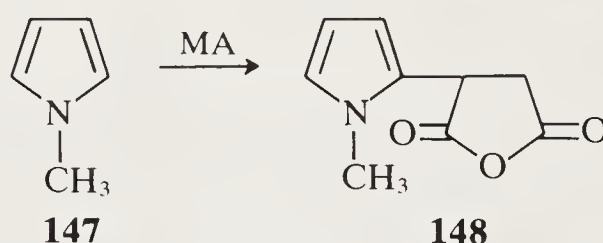
MA adducts formed from furan derivatives are generally labile and dissociate in solution. The extent of dissociation depends on the nature of



substituent on the furan ring. Higher temperature always favors the reverse reaction such that most adducts dissociate on melting if the furan component is volatile. This reversibility of the reaction has often been used advantageously for purification and for chemical modification in these and other systems (see Chapter 3). Although the reaction is reversible, the forward reaction occurs readily at lower temperatures ( $<120^{\circ}\text{C}$ ). By the proper choice of solvent, high yields of the solid adducts can be obtained.<sup>(23)</sup>

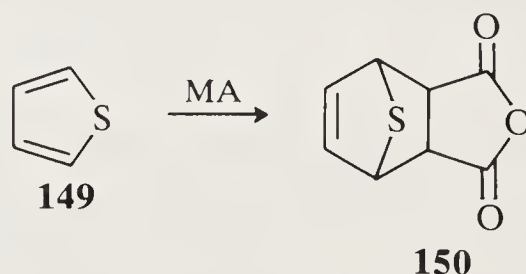
It may be of interest to note that not all dienophiles react with furan to give the DA adduct. Thus, furan and 2-methylfuran react with acrolein,<sup>(131)</sup> crotonaldehyde, methylvinyl ketone, and phenylvinyl ketone<sup>(132)</sup> to yield substitution products.

Pyrrole derivatives fail to give normal adducts and instead give substitution products as illustrated with *N*-methylpyrrole **147** below.<sup>(133–135)</sup>

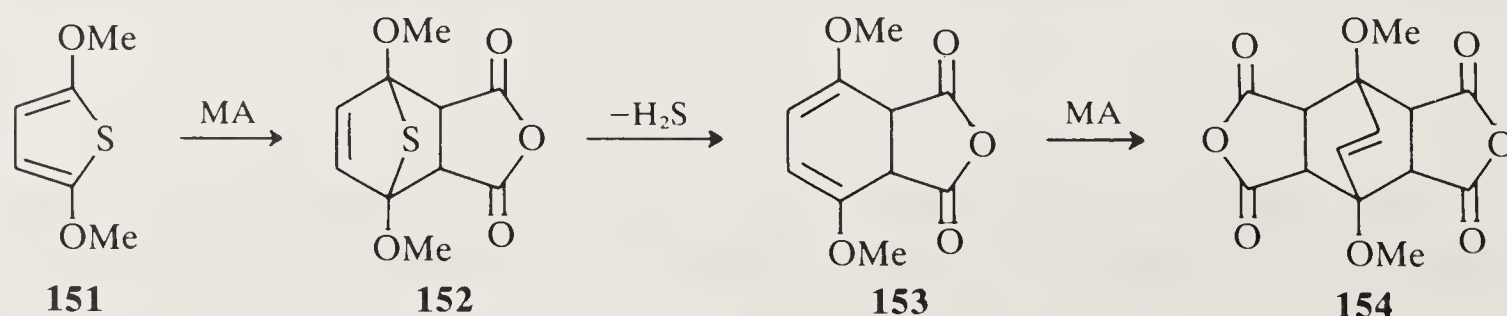


However, there is a report claiming normal Diels–Alder adduct from *N*-isobutylmaleimide.<sup>(136)</sup> Furthermore, there are recent reports of *N*-substituted pyrroles forming normal adducts with esters of acetylenedicarboxylic acid.<sup>(43,137–141)</sup> However, for our purpose here, maleic anhydride may be expected to give primarily substitution products.

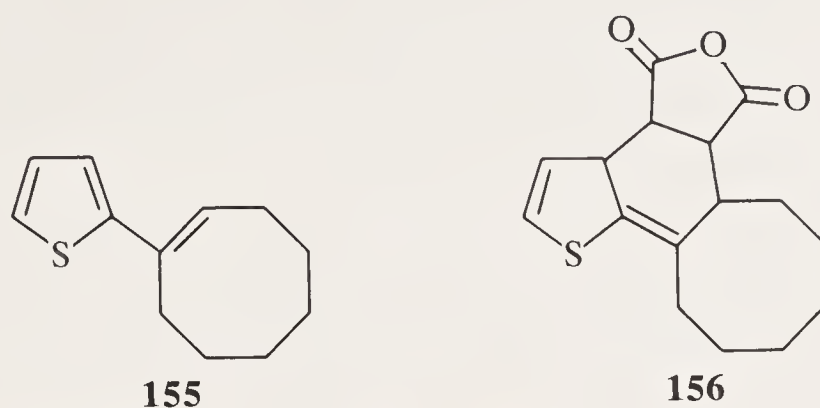
Thiophene **149** until recently was believed not to react with maleic anhydride. This lack of reactivity was ascribed to the high aromatic nature of thiophene. Recently, Kotsuki *et al.*<sup>(142)</sup> have found thiophene to form 37–47% of the *exo* product **150** at 15 kbars pressure. The mechanistic implications of high pressure are discussed later. The yield of the adduct was also shown to depend upon temperature and on the nature of the solvent.



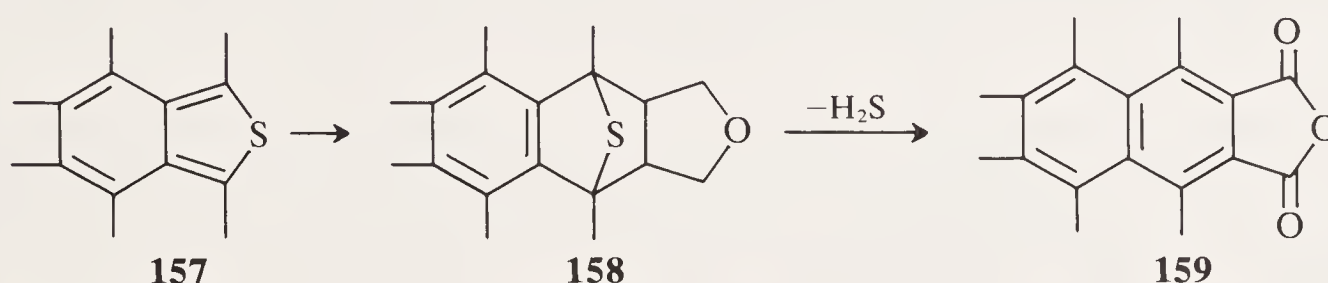
Baker *et al.*<sup>(143)</sup> have reported the reaction of 2,5-dimethoxythiophene **151** in refluxing xylene to form the normal adduct, which on loss of  $\text{H}_2\text{S}$



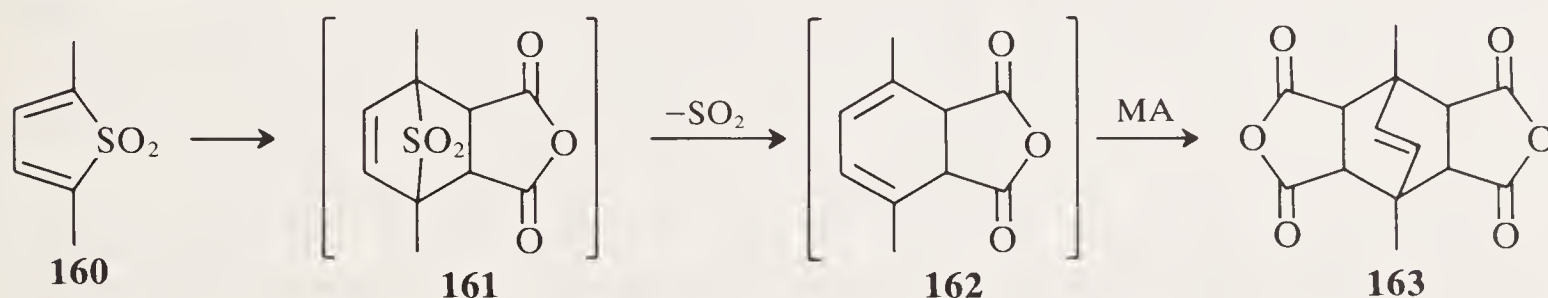
during the reaction added another mole of MA to form the bicyclic compound **154**. On the other hand, 2-vinylthiophene derivative **155** reacts with MA to give adduct **156**,<sup>(144)</sup> resulting from the participation of external double bond. Thus, the similarity of reaction of furan and thiophene ring is obvious.



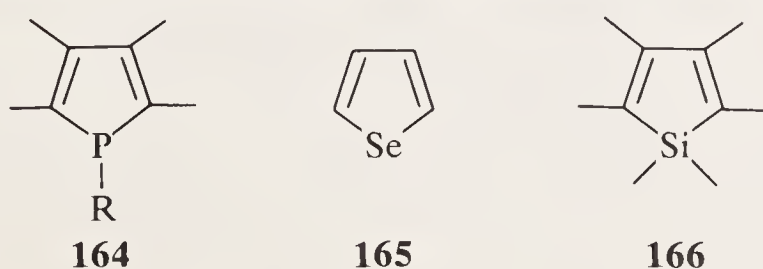
Like the isobenzofuran analogues, some isobenzothiophene **157** derivatives do react with maleic anhydride in a normal fashion. From these thiophene derivatives **158** aromatization is readily accomplished by the loss of  $\text{H}_2\text{S}$  either thermally<sup>(145)</sup> or with an acid catalyst when the sulfur bridge is not removed easily.<sup>(146)</sup>



Thiophene 1,1-dioxide **160** reacts with 2 moles of maleic anhydride with the consequent loss of  $\text{SO}_2$ . Here, loss of  $\text{SO}_2$  from the primary adduct **161** appears to give a new diene as illustrated below<sup>(148,149)</sup>: Unsubstituted thiophene-1,1-dioxide was reported to give a dimer which added MA after the loss of  $\text{SO}_2$ .<sup>(205)</sup>

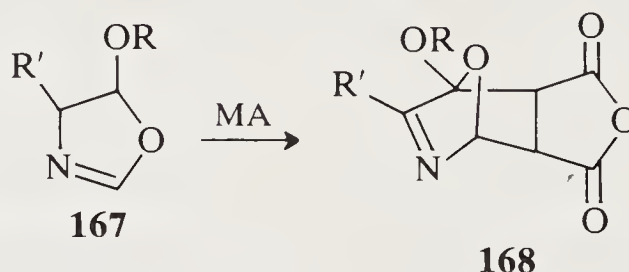


Diene reactivity has also been observed in other five-membered heterocycles such as phosphole **164**,<sup>(150,160)</sup> selenophene **165**,<sup>(151)</sup> and silacyclopentadiene **166**.<sup>(152)</sup> Of the above examples only in selenophene **165**



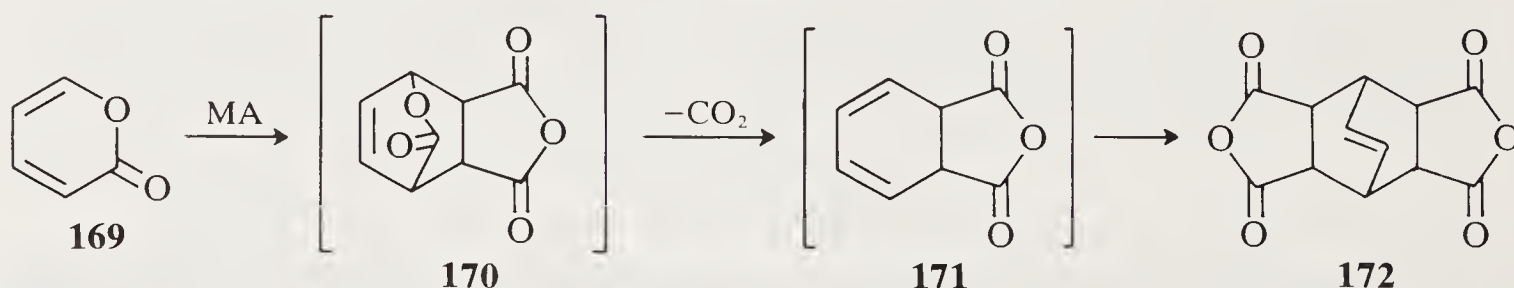
does the primary adduct readily lose 1 mole of  $\text{H}_2\text{Se}$  to generate a new diene which adds another mole of the dienophile analogous to the thiophene and the thiophene dioxide derivatives shown earlier.

Among the five-membered heterocycles containing two heteroatoms, oxazole derivatives and imidazole derivatives have been reported to react. Matsuo and Miki<sup>(155)</sup> have shown that the bicyclic adduct **168** from oxazole derivative **167** can be isolated as *endo* and *exo* isomers. With unsubstituted oxazole the adduct undergoes further reaction.<sup>(153,154)</sup>

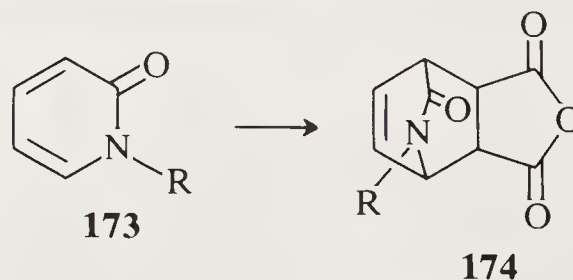


#### 4.3.6.2. Six-Membered Heterocycles

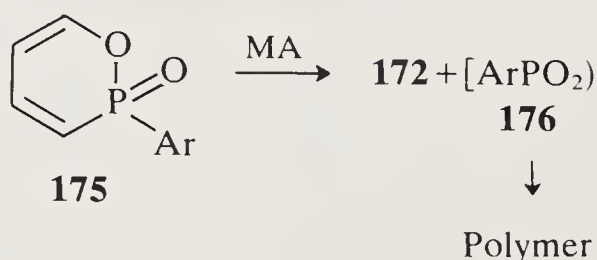
Coumaline ( $\alpha$ -pyrone) **169** forms a diadduct **172**. This apparently results from the initial diene adduct **170** losing  $\text{CO}_2$  to generate a new diene **171**



which also participates in the reaction.<sup>(156,157)</sup> The corresponding lactam **173**, however, does form a stable monoadduct **174**.<sup>(158,224)</sup> Stereochemically, the adduct has been assigned *endo* geometry.



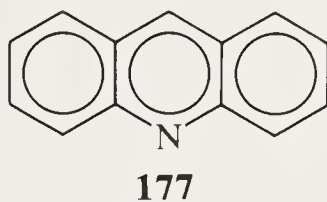
Recently, Sigal and Loew<sup>(159)</sup> have examined the reactions of the phosphorus analogue of  $\alpha$ -pyrone. On heating with MA at  $140^\circ\text{C}$  **175** gave **172** and a polymer of the phosphorus residue **176**. No intermediates were isolated.



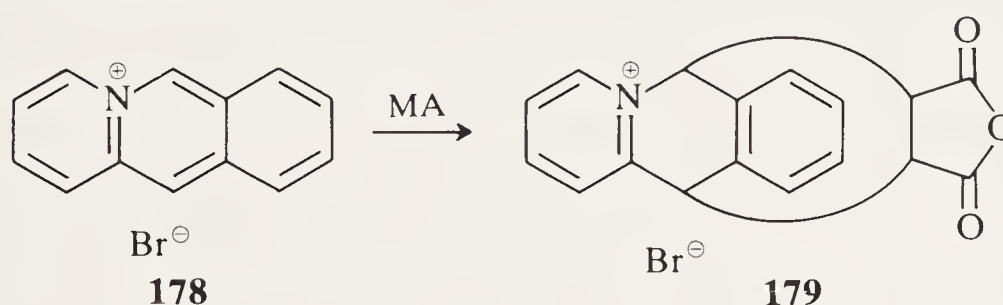


However, the DA reaction is analogous to that of **169** with different fates of residues split from the intermediate.

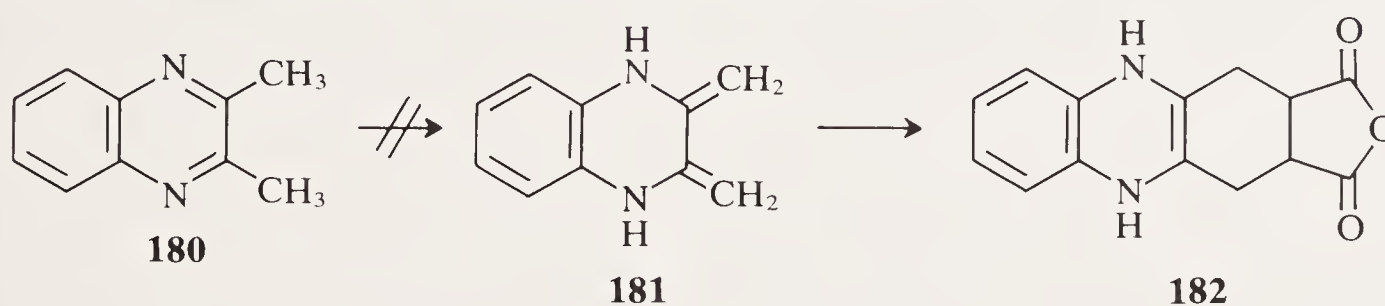
2-Styrylquinoline reacts with MA to give an ionic maleate salt corresponding to inclusion of 1 mole of water.<sup>(27)</sup> Acridine **177** which resembles



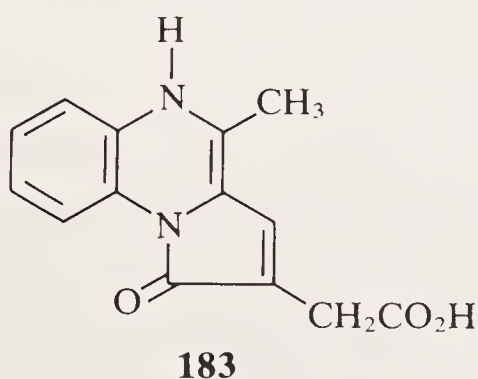
anthracene fails to react with MA. It may be noted that in **177**, the nitrogen atom is in the *meso* (–9) position of the anthracene analogue. In an unusual nitrogen heterocycle **178**, where the nitrogen atom is not in the *meso* position, Bradsher and Soloman<sup>(161)</sup> have shown that the reaction with MA does proceed in high yields to give **179**.



Schonberg and Mustafa<sup>(162)</sup> had originally formulated the product of 2,3-dimethylquinoxaline **180** with MA incorrectly as **182**.

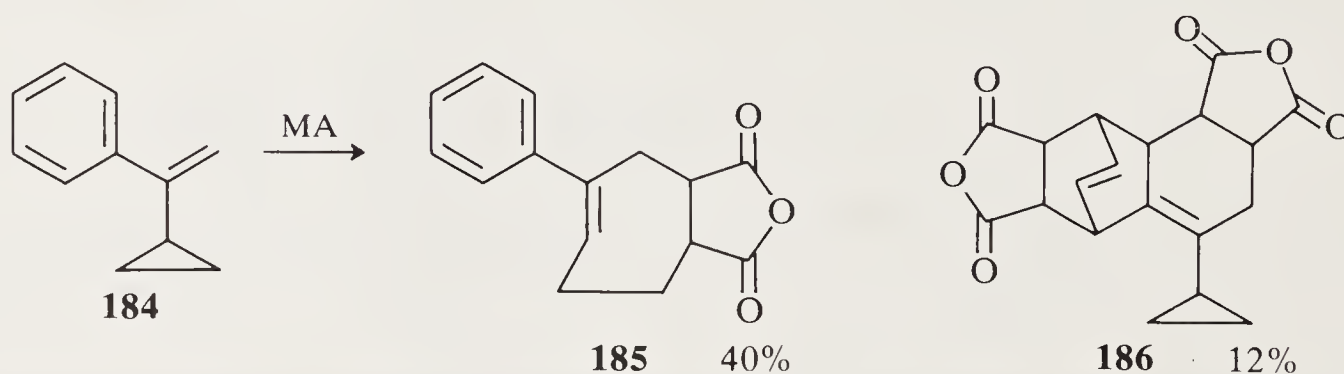


Their assignment was based on lack of reactivity in the monomethyl and nonalkylated derivatives of quinoxaline. However, Bird and Cheeseman<sup>(163)</sup> and Taylor and Smakulka Hand<sup>(164–166)</sup> have clearly shown that the reaction is more complex and gives the following product **183**. Thus, clearly the tautomeric structure **181** does not participate as a diene, as originally thought.

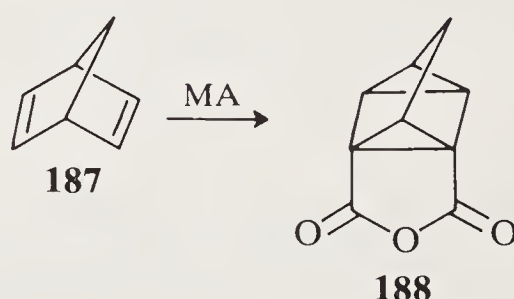


### 4.3.7. Miscellaneous

So far the systems under consideration for the Diels–Alder reaction with MA were conjugated dienes or systems that could give rise to diene intermediates. The latter could be generated, as we saw, by isomerization, tautomerization, pyrolysis, or even as the result of DA reaction when in some cases the primary products are unstable. In addition, there are some cases where a double bond in the diene may be replaced by a cyclopropane ring. An example of this is the vinylcyclopropane derivative reported by Sarel and Breuer.<sup>(167)</sup> They found  $\alpha$ -cyclopropyl-styrene **184** to react with MA. Two main products were obtained. Product **185**, obtained in a 40% yield, resulted from participation of the vinylcyclopropane unit in an apparent 1,5 addition process. The other product, **186**, results from participation of the styrene unit in the fashion discussed earlier.



Homodiene such as bicycloheptadiene **187**, although not conjugated, does enter into DA reaction with MA. Unlike the usual process where only two new bonds form at the expense of two  $\pi$  bonds, here three new bonds are formed by expending three  $\pi$  bonds. Thus **187** reacts with MA to give **188**.<sup>(168)</sup>



## 4.4. STEREOCHEMISTRY AND THE RETRO DIELS–ALDER REACTION

Earlier in this chapter, a mention was made of the steric requirements of the diene reaction. It was shown that by virtue of rotation around a C–C single bond, an equilibrium can exist between a cisoid and a transoid isomer. Only the cisoid form is able to participate in the reaction. Transoid dienes are less reactive and generally give rise to polymers in preference to the DA



adducts. In cyclic systems where the transoid configuration is locked, either no reaction occurs or rearrangement leading to a cisoid conformation occurs before the DA adduct formation. Thus, to participate in this reaction, a diene should be in a cisoid conformation or should be able to achieve that geometry.

Stereochemistry is an important tool for the understanding of reaction mechanisms as indicated by Martin and Hill.<sup>(77)</sup> However, before the steric course of the reaction can be used as a guide to the mechanism of the DA reaction of MA, a number of relevant factors have to be considered including<sup>(77)</sup>:

- (i) The MA adduct of anthracene, furan, fulvenes, etc. are known to dissociate into components. This reversibility may have an effect on the stereochemistry of the product.
- (ii) A kinetically controlled adduct forms more readily than the thermodynamically controlled adduct, generally. However, when both are formed simultaneously, they give erroneous information that the reaction gives a mixture of isomers. Only a kinetically controlled reaction giving a 1 : 1 adduct can give meaningful information about the steric course of the reaction.
- (iii) Dienophiles, such as maleates, can isomerize during the reaction to more stable fumarates. If the rates of isomerization versus adduct formation are competitive, the reaction may appear to be giving a mixture of isomers. Also, when the double bond in the newly formed ring is capable of migrating, erroneous stereochemical information may result.<sup>(169,170)</sup>

In addition, before the routine use of instrumentation such as gas–liquid chromatography, infrared spectroscopy, nuclear magnetic resonance spectrometry, etc., the identity of components and compositions were determined by isolation. The latter involved the problems of separating compounds of closely related properties. This often explains conflicting and inaccurate data published in the literature. The modern techniques of determining compositions have resolved some of these problems.

During the study of the diene synthesis, it was observed quite early that the reaction exhibited pronounced steric selectivity. Through the efforts of Alder and Stein<sup>(171)</sup> some confirmed generalizations have evolved which are useful guides.

*Cis Principle:* The addition of a dienophile to a diene is a purely *cis* addition. Thus, the adduct from anthracene and maleic anhydride (a *cis*-dienophile) is *cis*-anhydride. Fumaric acid (a *trans*-dienophile), on the other hand, adds to yield a *trans*-dicarboxylic acid.<sup>(23)</sup>

Thus, the original geometry in the dienophile is retained. Under kinetically controlled conditions, there are no exceptions to this rule and many examples

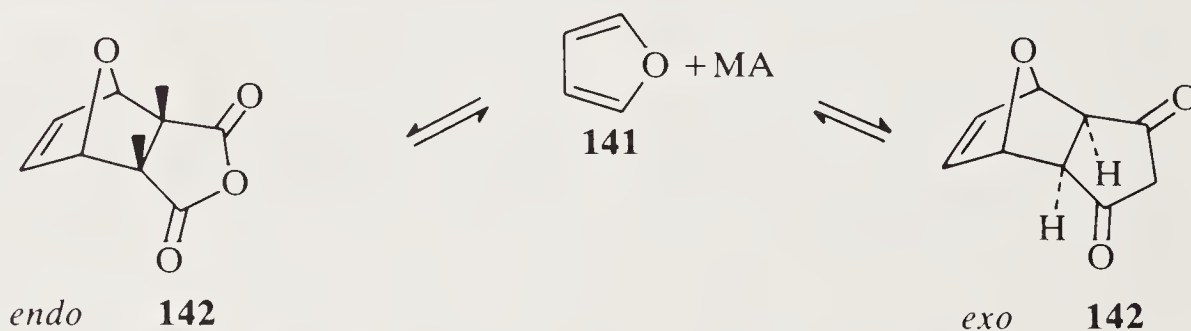


demonstrate this rule.<sup>(77)</sup> Unequivocal evidence for the stereochemical fate of substituents in the dienes are not as prevalent because only a few cases have been examined thoroughly. However, Alder and Stein<sup>(171)</sup> have shown in their study of 1,4-disubstituted dienes that, without exception, the adduct forms with retention of relative configuration of the substituent in 1 and 4 position of the diene.

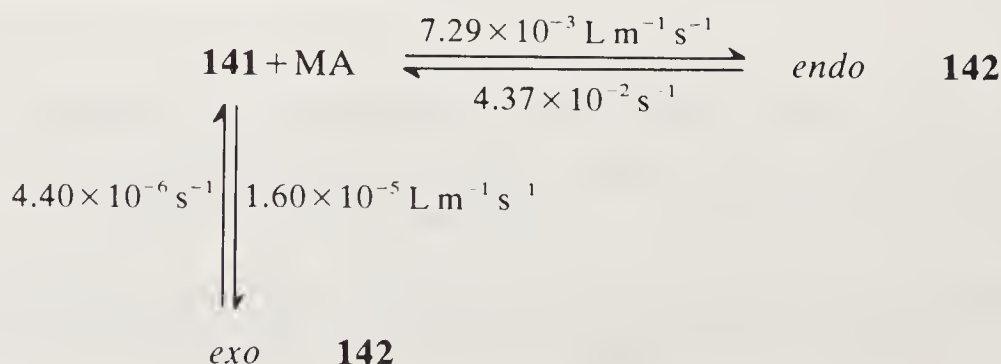
**Endo Rule:** When a cyclic diene and a dienophile are allowed to react, two possible products may be formed as illustrated with cyclopentadiene and MA earlier and with furan and MA below.

Generally only one of them, i.e., the *endo*-isomer is realized. With the cyclopentadiene only 1.5% of the *exo*-isomers are obtained. The explanation for the *endo* preference given by Alder and Stein is interpreted as follows: The diene and dienophile are preoriented in a sandwichlike structure. The transition state forms in such a way as to allow "maximum concentration" of double bonds. The suggested maximum concentration includes the  $\pi$  system as well as the activating groups.

During the reaction of furan **141** with maleic anhydride or maleimide, this rule on a cursory examination appears to be violated (but see below).



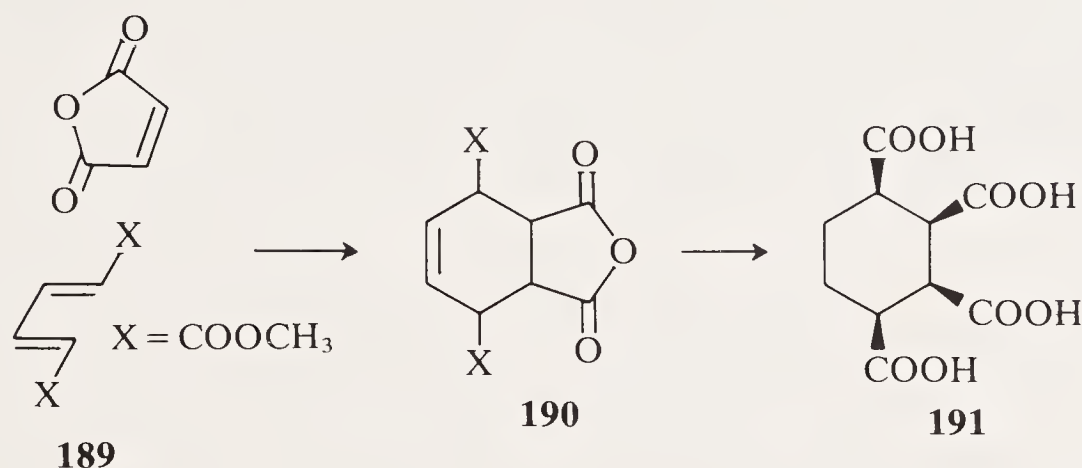
For a long time there was an uncertainty about the stereochemistry of furan–MA adduct because of redissociation of product and reassociation of the components. Diels *et al*<sup>(118)</sup> had originally formulated the adduct as *endo*. Woodward and Baer<sup>(172)</sup> later showed that the adduct was *exo*. However, Anet<sup>(173)</sup> contended that the *exo*-isomer formed in a kinetically controlled step was twice as fast as the *endo*. This was even claimed to be probably the first exception to the *endo* rule. However, in a recent NMR study, Lee and Herndon<sup>(174)</sup> have shown that the initial rate of formation of *endo*-adduct is 500 times faster than that of the *exo*-adduct. They have calculated the equilibrium data as shown below.



The isolated product was shown to be *exo* as decided earlier by Woodward and Baer.<sup>(172)</sup> By assuming comparable entropies of activations, it was shown that *exo* formation required 3.8-kcal higher activation energy but was 1.9 kcal/mole more stable.

Thus, it was not only conclusively shown that the *endo* product was formed in a kinetically controlled step as assumed before, but also the importance was shown of running the reaction under controlled conditions for determining the stereochemical course of the reaction.

Similarly, a mixture of *endo*- and *exo*-adducts is formed during the reaction of dimethyl maleates with cyclopentadiene **47**.<sup>(175)</sup> As pointed out earlier, the cisoid form in the open-chain dienes is quasicyclic and hence the “*endo* rule” may be tested against that. An interesting case is the reaction of MA with dimethyl *trans*-muconate **189**. High yields of a product **190** containing all *cis*-carboxylic groups are obtained.<sup>(176)</sup> The *cis* geometry was verified by alternate synthesis of the hydrogenated product **191**.<sup>(177)</sup>



It has been shown so far that the *endo* product is formed in a kinetically controlled step. It is the favored product at lower temperatures. Furthermore, the *endo/exo* ratio may be affected by the polarity of the solvent. By studying the reaction of cyclopentadiene and acrylates, Berson<sup>(178)</sup> has shown that solvents of high polarity favor the *endo* product. This is so, it is argued, because the latter goes through a transition state which is more polar than that for the *exo* product. Certain Lewis acids<sup>(179)</sup> which catalyze the DA reaction are also shown to affect the *endo/exo* ratio of the product from diethyl maleate and dimethyl maleate with cyclopentadiene (see Table 4.8).

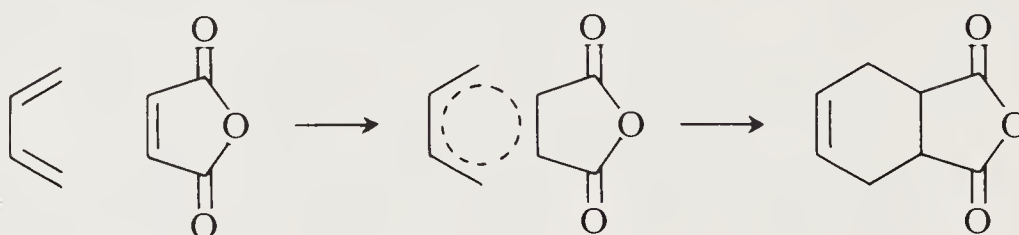
When dealing with a reaction preferring one isomer over the other, it is important to remember that only small activation energy differences are needed to change a reaction from nonstereospecific (1:1) to highly stereospecific.<sup>(179,180)</sup> However, given the number of factors affecting the steric selectivity such as catalysts,<sup>(179)</sup> solvents,<sup>(178)</sup> electrostatic field,<sup>(229)</sup> it is difficult to predict *a priori* the steric outcome of a reaction. Furthermore, the nature of the diene may often alter the course of the reaction.<sup>(230)</sup>



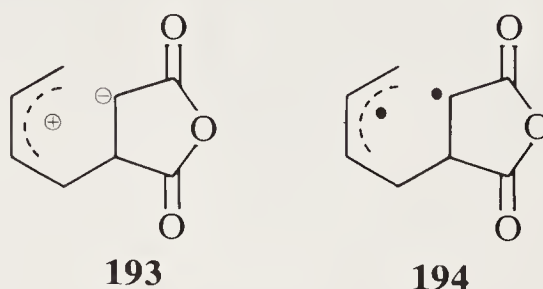
## 4.5. MECHANISM

As outlined earlier, in the Diels–Alder reaction, two  $\pi$  bonds are expended to yield two new  $\sigma$  bonds. This raises the following distinct possibilities about the mechanism of the reaction<sup>(8,232)</sup>:

1. In a concerted step, the new  $\sigma$  bonds may be formed in a multicenter mechanism. In this case, no intermediates would form, only a transition state. Thus, there would be only one activation barrier in the energy profile.



2. The overall reaction may be a two-step process. In the first step a distinct intermediate may form. The latter may be
  - (a) a dipolar or zwitterionic intermediates **193**.
  - (b) a diradical intermediate **194**.



In either case, there would be two activation barriers in the energy profile.

Furthermore, when dealing with a diradical, one should also take into account the possibility of paired (singlet) and unpaired (triplet) states.

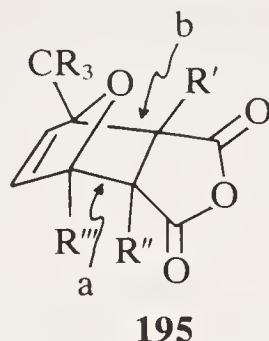
The pure *cis* addition of the reactants can be easily explained by a one-step concerted mechanism. However, an added restriction becomes necessary to explain the other two intermediates. Here, a rotation around a single bond in the intermediate may alter the geometry of the product. For this not to happen, a partial-bond formation may be invoked. Thus, in the case of a zwitterionic intermediate **193**, only partial charges may be developed at the termini. Similarly, with the diradical form **194** only partial radical character may be invoked.

In a number of cases, e.g. fulvenes,<sup>(52–55,57)</sup> retro DA reactions have been well documented. It is found that the rate of isomerization of the adduct is not necessarily related to the rate of the reaction. This suggests that the rearrangement of the adduct may involve breaking a bond, a necessary rotation around the bond, followed by reformation of the bond. It has been argued



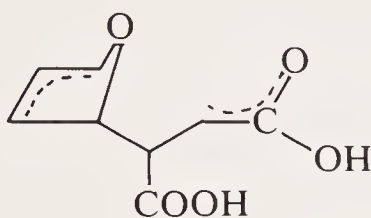
that since this may be the case in the retroreaction, by the principle of microscopic reversibility, it should also be the case in the forward reactions.<sup>(183)</sup>

Some effort has been spent to ascertain the validity of this hypothesis by the use of kinetic isotope effects in the retro Diels–Alder reaction. Seltzer<sup>(184,185)</sup> has estimated the effect of isotopes on decomposition of compound **195** which is an adduct of 2-methylfuran and MA. The primed R's in



compound **195** were variously hydrogen or deuterium. Based on his kinetic experiment, Seltzer concluded that the retroreaction must involve simultaneous breaking of bonds labeled a and b. This was therefore taken as a proof of simultaneous creation of these bonds during the adduct formation.

Gagnaire and Payo-Subiza<sup>(186)</sup> reported observation of a small amount of fumaric acid along with 2-methylfuran, maleic acid, and *endo-cis*-adduct on studying the retroreaction of compound **195**. This formation of fumaric acid which is a *trans* acid has been suggested an evidence of nonconcerted breaking of bonds a and b, and hence a nonconcerted formation of bonds a and b in the forward reaction. However, Shih and coworkers<sup>(187)</sup> have shown recently that fumaric acid is a product of a minor side reaction, and hence may not enter into the overall picture of the mechanism. (See also Ref. 232.) Furthermore, no mention was made by Gagnaire and Payo-Subiza<sup>(186)</sup> of the adduct(s) corresponding to 2-methylfuran and fumaric acid, which may be present in substantial amounts particularly if only one bond ruptured, allowing a rotation.

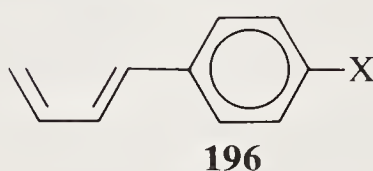


Similar results have also been reported by Van Sickle and Roden<sup>(188)</sup> in studying the kinetics of the reaction of deuterated butadiene and anthracene with maleic anhydride. They believe their results are consistent with a four-center transition state which is only a short distance from starting material along the reaction coordinate. This implies that the transition state resembles starting materials more than the product. Wong and Eckert<sup>(189)</sup> have also reached similar conclusions. Grieger and Eckert<sup>(190–192)</sup> and McCabe and Eckert<sup>(193)</sup> have examined reactions of a number of dienes with MA under high pressure. On examining  $\Delta V^\ddagger$  and solvent effects, they suggest that the

transition state should be more productlike. Thus, conclusions by these investigators may appear to contradict. However, Van Sickle and Roden,<sup>(188)</sup> in suggesting an early transition state, are describing only the electronic progress of the reaction wherein, typically, activation energies are low and reactions are exothermic—a classic description of an early transition state.<sup>(194)</sup> On the other hand, Eckert *et al.* are using activation volume which is a criterion for nuclear positions. Grieger and Eckert<sup>(191)</sup> and McCabe and Eckert<sup>(193)</sup> have further studied physical properties of the transition state and suggest that the latter is more compact in volume than the product. (See Table 4.6.) This is attributed to secondary interactions between nonbonding atoms in the transition state.

The suggestion of a compact transition state by Grieger, McCabe, and Eckert is interesting. In a multicenter reaction, a successful collision requires proper orientation of all the nuclei in question or a high degree of organization in the transition state. All such multicenter reactions, therefore, are characterized by high entropy of activation. Diels–Alder reactions, too, generally show high entropy ( $\Delta S^\ddagger > -25$  cal/deg mole) of activation.<sup>(8,193)</sup> Furthermore, relatively small changes in entropy between different DA reactions regardless of the absolute rate suggest a common concerted mechanism for many of these reactions.

DeWitt *et al.*<sup>(195)</sup> have studied the effect of substituents on the rate of the reaction between substituted 1-phenyl-1,3-butadiene **196** and MA. The



rates of these reactions were measured by isotope dilution techniques. They showed, using various *para*-substituents that the rate deviates from the Hammett equation if  $\sigma$  values are used for these substituents. Okamoto and Brown<sup>(196)</sup> later showed that the correlation improves significantly if  $\sigma^-$  values are used. Diene reactivity in the Diels–Alder reaction between 1-(*p*-substituted phenyl)-1,3-butadienes<sup>(196)</sup> and MA were also studied by Ottenbrite and Alston.<sup>(211)</sup> In their studies the *para* substituent (x) was methoxy, methyl, hydrogen, chloro, and nitro groups. It was shown that

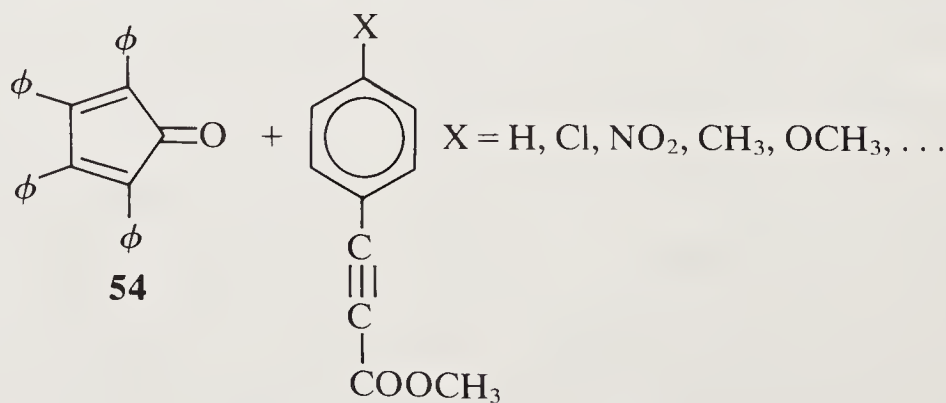




Table 4.6. Activation Parameters and Volumetric Relationships for Several Diels–Alder Reactions<sup>a</sup>

Reaction (solvent)	Activation energy (kcal/mol)	Activation volume (cm <sup>3</sup> /mol)	Partial molal volume at infinite dilution (cm <sup>3</sup> /mol)			
			Diene	Dienophile	Transition state	Adduct
1,3-Cyclohexadiene-maleic anhydride (dichloromethane)	11.4	−37.2	96.3	71.0	130	137.0
Isoprene-maleic anhydride (acetone)	14.0	−39.0	101.0	69.4	131	134.5
<i>trans</i> -1-Methoxy-1,3-butadiene-maleic anhydride ( <i>n</i> -butyl chloride)	10.7	−45.4	100.6	69.6	125	134.7

<sup>a</sup> Reprinted with permission from *J. Am. Chem. Soc.* **92**, 7149 (1970). Copyright © 1970, American Chemical Society.

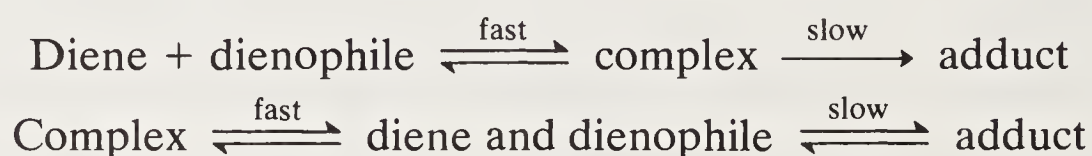
electron donating groups helped to stabilize the Diels–Alder reaction transition state and increase reaction rates. Similarly, Matthews and Becker,<sup>(197)</sup> studying the following Diels–Alder addition reaction between **54** and **197** showed that for the dienophile  $\sigma^+$  substituent constants gave better correlation. These observations fit the generally accepted mechanism that the diene is the electron donor and the dienophile the electron acceptor. This is because the  $\sigma^+$  value generally correlates well when the substituent enters into direct resonance interaction with the electron-rich center. (However, see Sect. 4.6 for examples with inverse electron demand.)

The Hammett reaction constant ( $\rho$  values) for DA reactions are small<sup>(181,197)</sup> showing relatively low sensitivity of the reaction to substituents. Since reactions involving charge centers, e.g., a zwitterion, generally show high sensitivity (large value), it may be assumed that no truly zwitterionic species exists as an intermediate. (However, low partial charges cannot be ruled out.)

Berson and coworkers<sup>(198,199)</sup> have reported that the addition of 9-phenylanthracene to MA is not affected by ferric-dipivaloylmethide. The latter is a known catalyst for singlet-triplet conversion. From this and other kinetic evidence on the stereochemistry of cyclopentadiene-acrylate adducts, Berson and coworkers argue that a diradical intermediate can be eliminated from consideration in the Diels–Alder reaction. Different products formed from photochemical versus thermal DA reaction may be considered as evidence of the absence of a triplet intermediate as well, although a singlet diradical cannot be ruled out.<sup>(181)</sup>

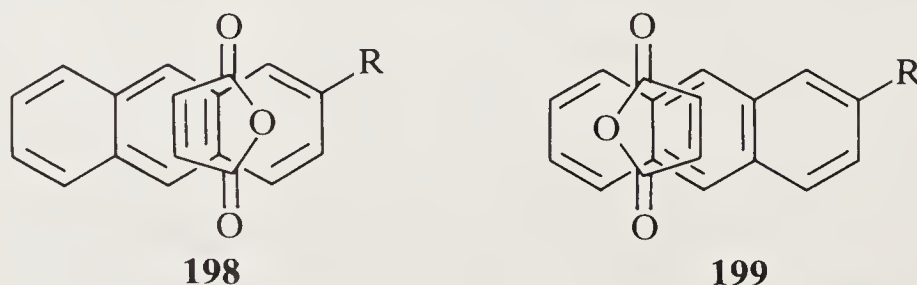


Another consideration is the formation of a charge-transfer complex as an intermediate. It is not difficult to think that some charge transfer occurs on the way to the transition state. A number of dienes form charge-transfer complexes with MA as well as other dienophiles. This is often evidenced by formation of transient colors. Experimentally, this can be determined spectroscopically. A detailed argument about this possibility would be difficult to entertain. Suffice it to say that according to Andrews and Keefer<sup>(200)</sup> it is impossible to distinguish kinetically between the following two mechanisms:



The mathematical difficulty is further compounded by the facts that electron-withdrawing groups in the dienophile and electron-donating groups in the diene assist the DA reaction as well as the formation of charge-transfer complexes. The effect of solvents has been shown to be the same for the diene reaction and charge-transfer complex formation as well.<sup>(201)</sup>

The above description suggests concerted or near concerted adduct formation. Woodward and Katz,<sup>(202)</sup> on the other hand, prefer formation of only one bond in the transition state; the rate-controlling step is proposed to be this bond formation. The geometric constraints necessary for the stereospecificity observed is explained by secondary attractive forces between electrons that are not necessarily associated with the primary bonding process. The origin of these is symmetry-controlled secondary-orbital interactions.<sup>(203,204)</sup> The latter explanation is popularly known as Woodward-Hoffman rules. The secondary-orbital interactions have been shown to have effect on the stereochemical preference of the Diels-Alder reaction. It is the basis of the empirically formulated *endo* rule of Alder. Furthermore, Kaplan and Conroy<sup>(111)</sup> have shown that during the reaction of 2-substituted anthracene with MA, the transition state containing the anhydride ring above the electron-rich aromatic ring **198** is more stable than the alternate possibility **199**. Similar secondary interactions have been claimed by Eckroth.<sup>(206)</sup>



So there seems to be a fair agreement on the overall mechanism, the main differences being in fine points. Thus, each of the proposed mechanisms has to rationalize the stereospecificity of the reaction. To do that, on one extreme are primary interactions leading to simultaneous bond formation of

two bonds and on the other extreme is one bond formed with the geometry fixed by secondary interactions. In other words, there is hardly a question that the reaction is concerted. However, the main difference is whether the transition state in a concerted mechanism is symmetric—i.e., do both  $\sigma$  bonds form simultaneously or is there a time lag involved? Liu and Schmidt<sup>(207)</sup> believe it to be asymmetric for the reactions of 1,4-disubstituted butadiene with 2,6-dimethylbenzoquinone. Taagepera and Thornton<sup>(208)</sup> have studied the transition state in the reverse DA reaction of 9,10-dihydro-9,10-ethanoanthracene. The transition state is claimed to be symmetrical or nearly symmetrical in this case.

Whether one agrees with the symmetric or asymmetric transition state, the secondary interactions are of great significance. This can be visualized by the application of the principle of conservation of orbital symmetry. According to the latter, a reaction is favored only when all the overlaps between the highest occupied molecular orbital (HOMO) of one reactant and the lowest unoccupied molecular orbital (LUMO) of the other are such that the overlapping lobes have the same sign. The two molecular orbitals of the dienophile (olefin) and three of the diene are shown in Fig. 4-1. Looking at the figure, an overlap between either the HOMO of olefin and LUMO of the diene or vice versa are allowed processes as shown in Fig. 4-2.

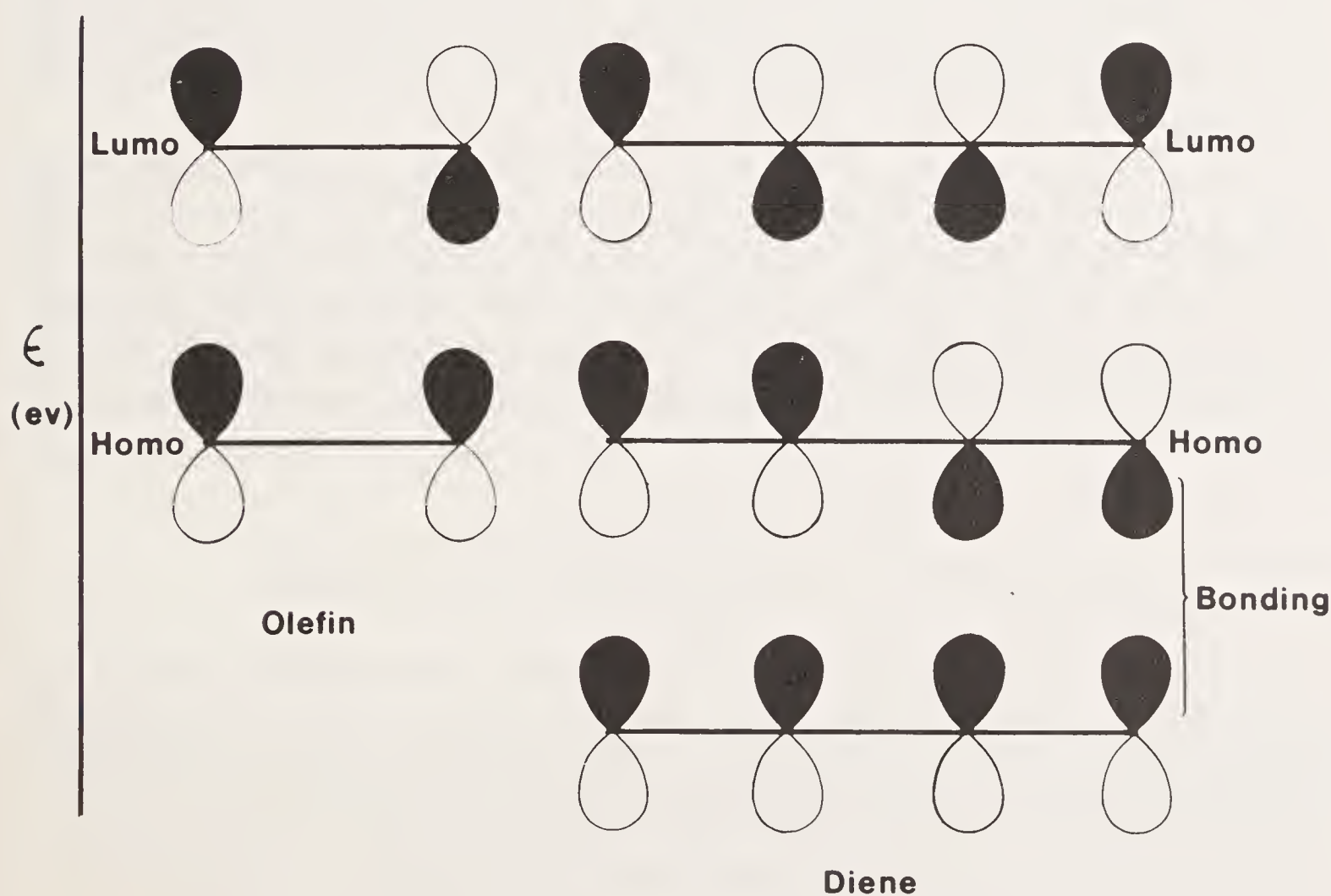


Fig. 4-1. Representative of the HOMO and Lumo of olefin and diene.



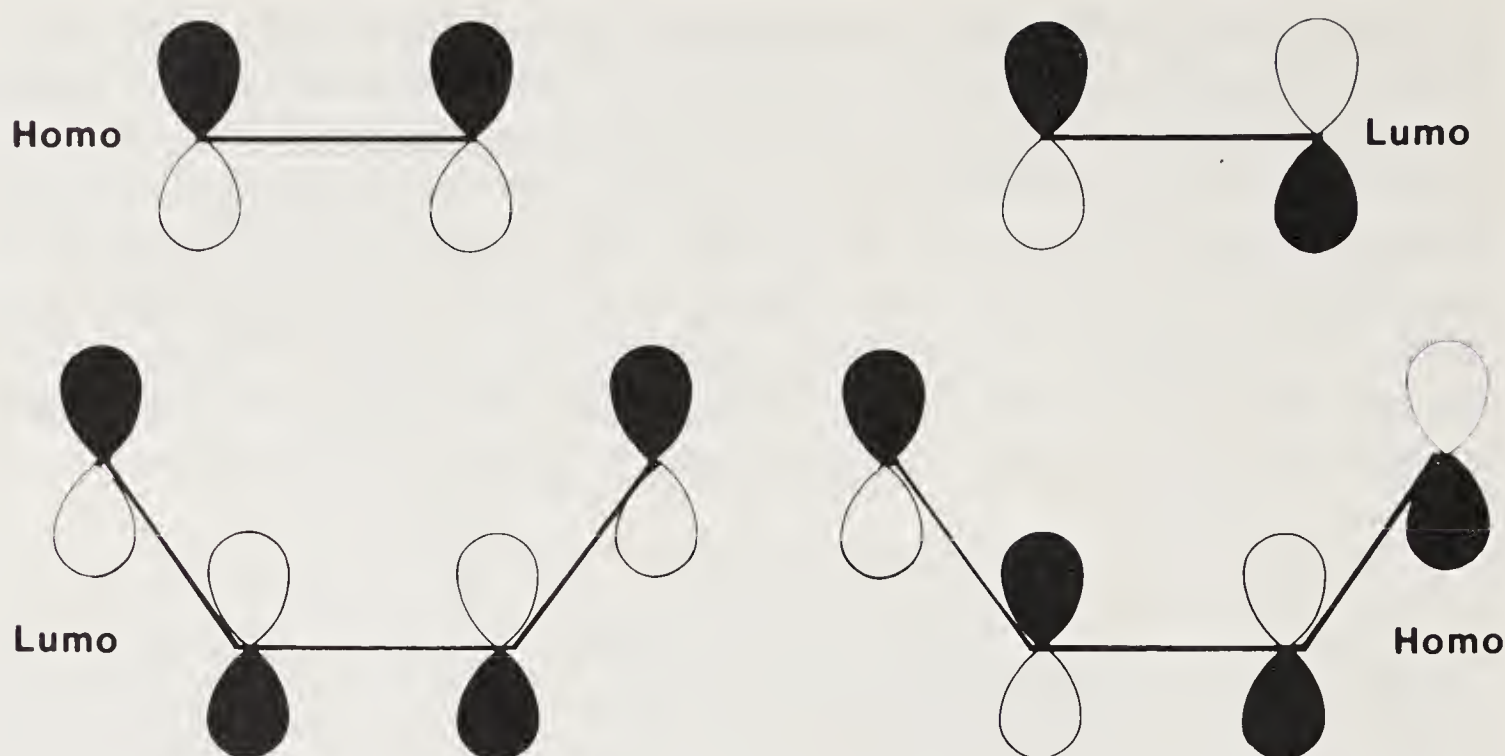


Fig. 4-2. Interaction between Homo (olefin) and Lumo (diene); Lumo (olefin) and Homo (diene).

The consequent stereochemistry as shown by the *endo* preference can be rationalized by nonbonded interactions, e.g., the carbonyl groups of maleic anhydride. For conjugation in the ground state, the partial orbital pictures of MA would suggest that the overlapping of the MA plane with that of the diene would provide a greater interaction and hence greater stability than in the alternate configuration where MA carbonyl groups do not interact with the diene.

It may be pertinent to add that a significant amount of theoretical work has gone into understanding and rationalizing the Diels–Alder reaction with a view to obtaining predictive value.<sup>(210,211)</sup> An interested reader is referred to a recent review by Sauer and Sustmann<sup>(232)</sup> where a detailed discussion on the mechanism of DA reaction is given. Reviews by Herndon<sup>(182)</sup> and the frontier molecular orbital approach by Houk<sup>(209)</sup> shed further light on the subject.

#### 4.6. REACTIONS WITH INVERSE ELECTRON DEMAND

As shown earlier, most of the kinetic data with substituted dienes and dienophiles support the contention that generally the diene is the electron donor and the dienophile the electron acceptor. However, a look at Fig. 4.2 suggests that either of the interactions shown below are allowed:

HOMO Diene: LUMO Dienophile

HOMO Dienophile: LUMO Diene



Table 4.7. Kinetics of DA Reaction of Various Dienophiles with Hexachlorocyclopentadiene and 9,10-Dimethylantracene in Dioxane at 130°C <sup>a</sup>

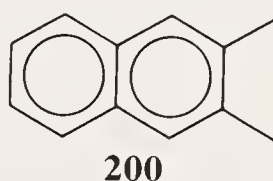
Dienophile	$k_2 \times 10^6$ (liter/mol s)	
	Hexachlorocyclopentadiene	9,10-Dimethylantracene
Cyclopentadiene	15 200	—
<i>p</i> -Methoxystyrene	1 580	50
Styrene	793	70
<i>p</i> -Nitrostyrene	538	602
2,3-Dihydrofuran	333	—
Norbornene	72	36
Cyclopentene	59	7.8
MA	29	1 410 000

<sup>a</sup> From Reference 213.

Thus, electron-poor dienes may be able to react with electron-rich dienophile. In 1949, Bachmann and Deno<sup>(212)</sup> first proposed such a possibility. Through the efforts of Sauer and Weist<sup>(213)</sup> such systems were proven experimentally. They used various dienophiles and studied their reaction kinetics with (a) hexachlorocyclopentadiene as an electron-poor diene and (b) 9,10-dimethylantracene as an electron-rich diene. As shown in Table 4.7, a very clear demonstration of the phenomenon occurs.

## 4.7. CATALYSIS

Woodward<sup>(214)</sup> suggested the possibility of catalyzing the diene synthesis with *N,N*-diethylaniline and 1,3,5-trinitrobenzene although no experimental details were given. Others suggested acid catalysis but the increases in rate were small.<sup>(8)</sup> Yates and Eaton<sup>(215)</sup> showed that an adduct of 2,3-dimethylnaphthalene **200** with maleic anhydride could be obtained in 4 h at room



temperature using aluminum chloride. The same reaction required heating for 24 h at 100°C without the catalyst. A number of other Lewis acid catalysts, e.g.,  $\text{BF}_3$ ,  $\text{SnCl}_4$ , and the like, have also been mentioned in related systems.

The use of a catalyst also allows the reactions to be run at lower temperatures. As a consequence, certain dienes, e.g., 2,3-dichlorobutadiene and

2,3-dibromobutadiene, which were thought not to participate in the DA reaction in absence of a catalyst because they polymerized too rapidly, do yield DA adducts.<sup>(13)</sup>

Inukai and Kojima<sup>(179)</sup> have shown that in the reaction of dialkyl maleate with cyclopentadiene, the aluminum-chloride-catalyzed reaction yields a higher *endo/exo* ratio in the product (Table 4.8) than the uncatalyzed reaction. Similar results were also obtained with other dienophiles. A possible explanation is that by complexing with  $\text{AlCl}_3$ , the dienophiles are rendered more electrophilic and hence a rate enhancement is obtained. Stronger interaction in the transition state would favor the *endo* geometry.

As mentioned earlier, McMullen *et al.*<sup>(221)</sup> observed that 1,1'-bicyclobutenyl reacts with MA only in the presence of  $\text{CuCl}_2$ . It is not obvious if other catalysts were examined. If  $\text{CuCl}_2$  is unique, this work and the catalyst deserve a detailed study.

It is interesting to note that no catalysis by Lewis acids has been observed if no polar groups, such as nitriles, esters, and anhydrides, are involved.<sup>(78)</sup> Thus, some interaction between the activating group and the Lewis acid is suggested. Since both catalyzed and uncatalyzed reactions follow *cis* addition, i.e., they are stereospecific, no change in the mechanism is envisaged.<sup>(215)</sup> Anh and Seyden-Penne<sup>(216)</sup> have provided a perturbational treatment to the catalyzed Diels–Alder reaction. On assuming that the mechanisms are not different and that the primary modes of a Lewis acid during the reaction is complexation with the polar groups, excellent agreement between experimental results and theoretical prediction is observed.

Table 4.8. *Endo/Exo* Ratio<sup>a</sup> of the Products from the Reaction of Cyclopentadiene with Dialkyl Maleates<sup>b</sup>

Dienophile	Solvent	Catalyst	Reaction time (h)	Ratios	
				<i>Endo</i>	<i>Exo</i>
Diethyl maleate	Benzene	—	14	73	27
	Benzene	$\text{AlCl}_3$	1	96	4
	Benzene	$\text{AlCl}_3$	2	95	5
Dimethyl maleate	Dioxane	—	4	72	28
	Benzene	—	5.0	73	27
	Benzene	$\text{AlCl}_3$	1.0	94	6
		$\text{AlCl}_3$	2.0	94	6

<sup>a</sup> Determined by gas–liquid partition chromatography.

<sup>b</sup> Reprinted with permission from *J. Org. Chem.* **31**, 2032 (1966). Copyright © 1966, American Chemical Society.



## 4.8. EFFECT OF PRESSURE

It was pointed out earlier that a highly organized transition state is necessary for the DA reaction. Through the work of Eckert and co-workers<sup>(190–193)</sup> it has been shown that both  $\Delta V^\ddagger$  as well as  $\Delta V_{rxn}$  are negative for the reaction. Such systems are well known to be favorably affected by pressure. Johns and coworkers<sup>(100)</sup> have demonstrated this very nicely in case of the reaction of MA with naphthalene<sup>(111)</sup> as shown in Sect. 4.3.5 on aromatics. Also, thiophene **149** was until recently believed to be unreactive. However, through the high-pressure work of Kotsuki *et al.*<sup>(142)</sup> the adduct has been made with thiophene. From the foregoing, it is easy to see that very high pressures can be employed to accelerate the DA reaction. In a recent review, Axano and LeNoble<sup>(194)</sup> have surveyed activation volumes of a number of diene reactions with MA for those interested in high-pressure synthesis aspects.

## 4.9. EPILOGUE

Since the discovery of the DA reaction nearly 50 years ago, it has come to be understood in much greater detail. Admittedly, there are minor differences in views about the exact events along the reaction coordinate, but this in no way undermines the achievements of this reaction. The unique ring-closure aspect of the reaction has not only provided a gateway to the synthesis of a number of natural and synthetic products but has also given a number of commercially useful products. Of the many MA derivatives made with dienes, those from butadiene, isoprene, and hexachlorocyclopentadiene are probably the most popular. They are used in the manufacture of fire-resistant polyesters.<sup>(5)</sup> The uniqueness of MA as a starting material for biocides is well documented.<sup>(6,217)</sup> DA adducts of MA have been employed as commercially useful herbicides, insecticides, pesticides, and fungicides (see Chapter 1).

MA adducts of natural unsaturated acids and esters, such as linoleic and abietic, have found use in modified drying oil especially in paint, varnish, and printing industries due to their rapid drying characteristics.<sup>(3,4)</sup> Monomers and polymers made from terpenes and MA have also been used. Esters of DA adducts have also been utilized as plasticizers. An enormous amount of patent activity which can hardly be touched in such a work attests to the usefulness of the DA reaction of MA in commercial products.

Furthermore, we also touched on the role MA has played in pharmaceutical chemistry. In the synthesis of new derivatives of steroids and other natural products it has proved useful. Synthetically, it was seen that the DA reaction of MA can be used to prepare many new intermediates. The retro



Diels–Alder reaction has been usefully employed to protect the diene function when other groups in the molecule are being manipulated. This has resulted in synthesis of products from dienes as well as MA—the possibilities are limitless here.<sup>(218)</sup> Analytically, the DA reaction has been used to determine presence of *cis*-conjugated dienes (with caution).<sup>(219)</sup>

Thus, if one were to characterize the scope of usefulness of this reaction of MA it would be catholic. This, of course, describes the past. The universality and versatility of this compound has hardly been exhausted.

# 5

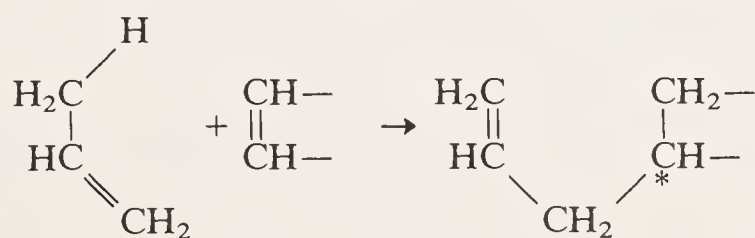
## ENE REACTION

### 5.1. INTRODUCTION

In addition to the famous Diels–Alder reactions, another important contribution of Kurt Alder is the systematic investigation of the ene reaction. The reaction of MA with olefin compounds was known, however, before the first paper by Alder and coworkers.<sup>(1)</sup> The reaction of unconjugated olefins with MA had represented some patent activity.<sup>(2–4)</sup> The products of the reactions had begun finding applications in the paint, varnish, coatings, and ink industries. Some effort had also started in understanding the process, e.g., Bickford *et al.*<sup>(5)</sup> had recognized that methyl oleate reacted with 1 mole of MA to yield an adduct with one double bond. They also recognized, at least qualitatively, the difference in the reaction of 2 moles of MA with methyl linoleate (see text). However, the initial work was less clearly understood primarily due to the lack of more sophisticated analytical techniques and instrumentation. Higher temperatures needed for the reaction often produce side reactions and thus make understanding difficult. As will be seen later, the formal similarity of the ene reaction of MA to those of other reagents such as formaldehyde and sulfur trioxide<sup>(6)</sup> as well as their relation to the related processes such as the DA reaction had to be recognized.

### 5.2. DEFINITION

The ene reaction was recognized by Alder *et al.*<sup>(13)</sup> to be “an indirect substituting addition.” In general, it involves the reaction of an olefin with an allylic hydrogen (ene) with another olefin (enophile), e.g., MA. As a result of the reaction a new bond forms between two unsaturated carbons and the allylic hydrogen transfers to the enophile through a cyclic transition state.

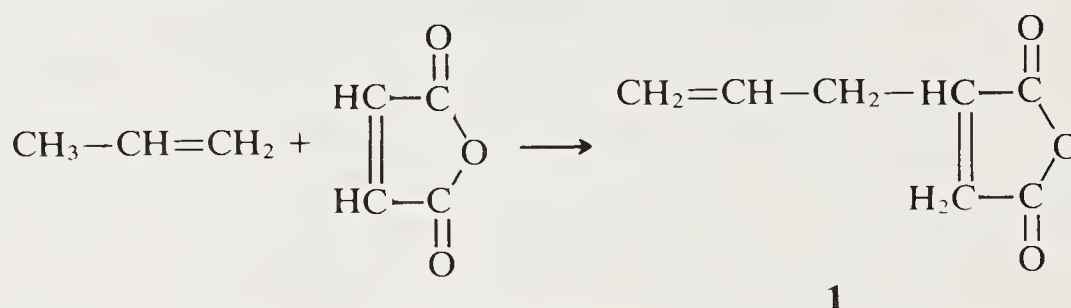


The necessity of an  $\alpha$ -hydrogen for the reaction has been well demonstrated.<sup>(96)</sup> The reaction creates an asymmetric center shown with an asterisk above.

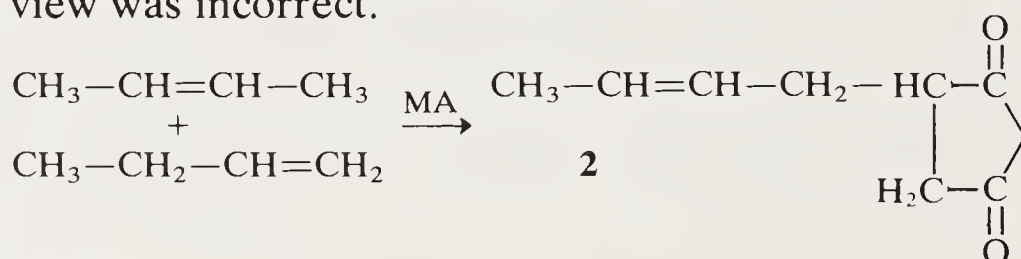
## 5.3. REACTIONS OF MA WITH VARIOUS OLEFINS

## 5.3.1. Aliphatic

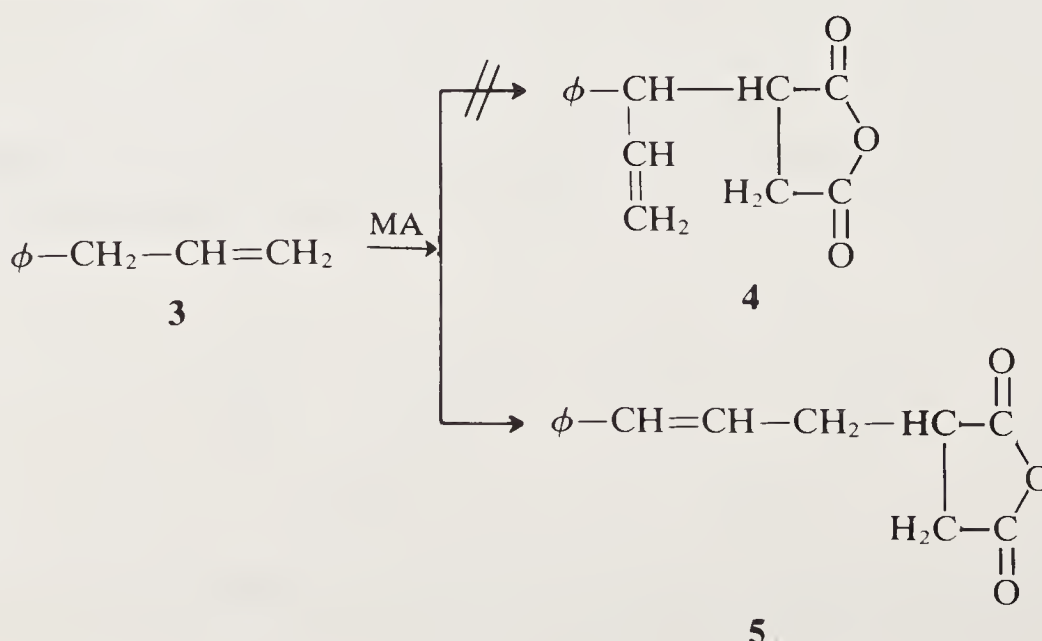
Alder *et al.*<sup>(1)</sup> were the first to study the scope of the ene reaction. They observed that although ethylene did not react with MA at 220–230°C, propylene did. The latter, on heating in benzene solution with MA at 250°C in the presence of an inhibitor in a sealed apparatus, gave allylsuccinic anhydride **1**. The presence of allylic hydrogens were thus deemed necessary. On heating



a mixture of butene-1 and butene-2 with MA, crotylsuccinic anhydride **2** was reported to be the product. Alder *et al.*,<sup>(1)</sup> based on the understanding of the time that addition occurred from the allylic position, assumed that the product formed from butene-2. The fate of butene-1, which contains a secondary allylic position, was not certain by their proposal. However, as we will see shortly, that view was incorrect.

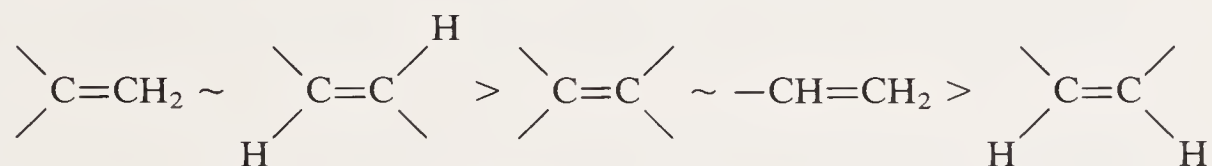


The case of allylbenzene **3** is of historical importance. The original mechanism based on allylic attack would have predicted **4** to be the product—instead **5** was obtained.<sup>(1,15)</sup> This led to the proposal of the cyclic transition state as we shall see later.





Generality of the reaction has been well documented. Some of the works leading to various alkenylsuccinic anhydrides (ASA) have been summarized (Table 5.1). It appears that yields improve to some extent with internal and 2-alkyl-1-olefins. This has been taken advantage of in a number of commercial products, where mixtures of olefins such as polyisobutylene oligomers and olefins produced from cracked hydrocarbon have been reacted with MA. Unusual properties of these type of products are thus made reasonably available. The reactivities for the open-chain olefins are<sup>(11,47)</sup>:



Methyl oleate **6** was among the first unsaturated esters to be examined by Bickford *et al.*<sup>(16)</sup> The reaction was conducted at 220°C, under a carbon dioxide atmosphere for 2 h. A structure was speculated on, again, involving allylic hydrogen. An ozonolysis study of the reaction product gave no conclusive information. Ross *et al.*<sup>(17)</sup> showed, based on oxidation of the products, that the reaction produces a succinic acid derivative by first attack at either the 9 or 10 position of methyl oleate **6** with consequent migration of the double bond to the adjacent 10,11 or 8,9 positions, respectively.

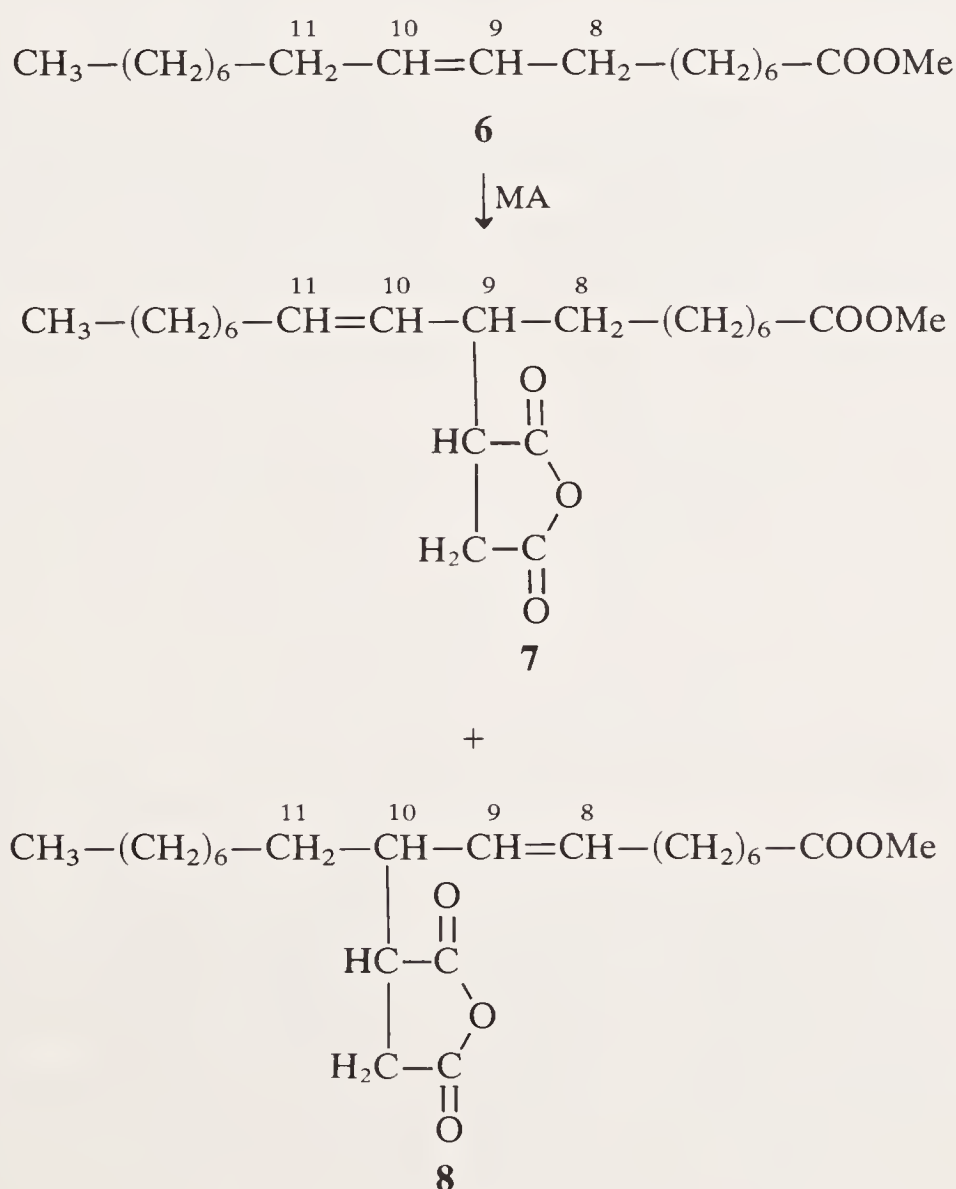
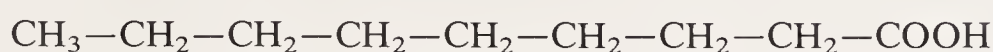


Table 5.1. Ene Reaction of MA with Aliphatic Olefins

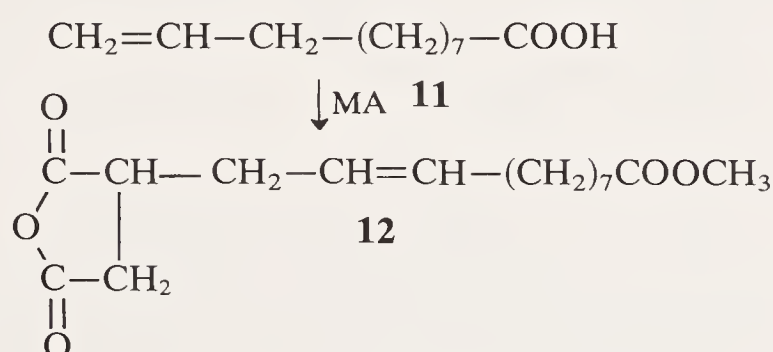
Olefin	Olefin/MA	Solvent	Temperature (°C)	Inhibitor <sup>a</sup>	Time (h)	Yield (%)	References
Propylene	1.86	Benzene	250	—	12	—	1
	1.9	Benzene	200	<i>t</i> BC		28.6	7
	2.0	Toluene		<i>t</i> BC	12	43.0	8
Butene-1	2.0	Toluene	200–300	<i>t</i> BC	2	60.0	8
Butene-2 (mixed)	2.0	Toluene	200–300	<i>t</i> BC	12–14	64.0	8
<i>cis</i> -Butene-2	—	—	—	—	—	20–30	9
<i>trans</i> -Butene-2	—	—	—	—	—	—	9
Isobutylene	1.75	—	—	—	—	23.8	1
	2.0	Toluene	230	<i>t</i> BC	1	78.0	8
	2.4	Benzene	180	—	—	64.0	9
<i>n</i> -Hexenes	—	—	—	—	—	good	1
<i>n</i> -Heptenes	—	—	—	—	—	good	1
Pentene-1	1.0	Toluene	190	HQ	24	55.0	6, 11
Hexene-1	1.0	Toluene	190	HQ	24	50.0	6, 11
			190	—	—	34.0	1
3-Methylbutene-1	1.0	Toluene	190	HQ	24	40.0	11
Pentene-2	0.82	Benzene	200	—	—	42.8	11
Allylbenzene	1.36	Benzene	170–175	—	—	48.0	1
	1.0	<i>o</i> -Dichlorobenzene	183	—	22	42–54	15
2-Methylbutene-2	1.0	Toluene	190	HQ	24	30.0	1, 11
2-Methylpentene-1	1.0	Toluene	140	HQ	5	9.0	11
2,3-Dimethylbutene-2	1.0	Toluene	140	HQ	48	25.0	11
		Benzene	200	—	—	43.5	1
2-Methyl- <i>trans</i> -pentene-3	1.0	Toluene	190	HQ	24	60.0	11
2-Methyl- <i>cis</i> -pentene-3	1.0	Toluene	190	HQ	24	3.0	11
Diisobutylene	1.05	Benzene	190	—	—	53.5	12
	5.0	—	200	—	5	91.9	102
Triisobutylene	—	—	200–210	—	24	60.0	12

<sup>a</sup> *t*BC = *t*-butylcatechol; HQ = hydroquinone.

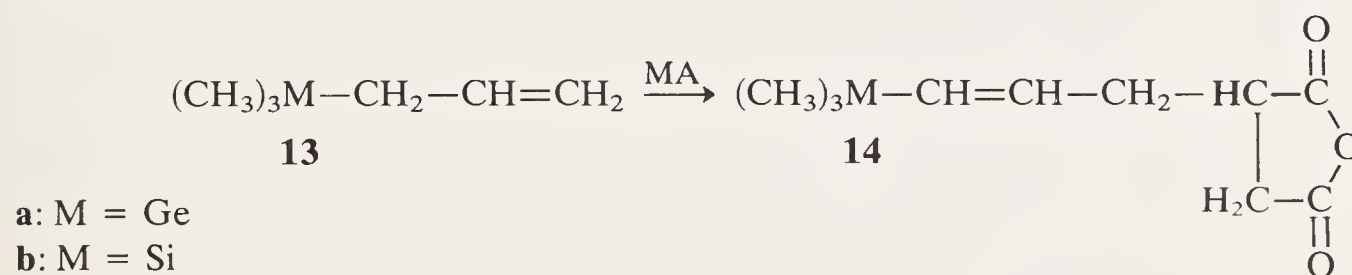
Rheineck and Khoe<sup>(18)</sup> reexamined the reaction with the help of oxidation and NMR studies. Among the products of oxidation they also found pelargonic acid **9** and azelaic acid **10**, suggesting that part of the double bond was retained in the 9,10 position of methyl oleate. Thus, at least in part, the product may arise from a competing radical mechanism.

**9****10**

Ross *et al.*<sup>(17)</sup> also studied the reaction of methyl undecylenate **11** with MA. The product was a mixture of diastereomers of **12** identified as the trimethyl ester derivative. Tamayo *et al.*<sup>(19)</sup> have also examined various unsaturated esters. Results of MA reaction with some unsaturated esters are shown in Table 5.2.



The general applicability of the ene reaction is exemplified in that aliphatic olefins containing a metallo substituent may also participate in the reaction. Laporterie *et al.*<sup>(21)</sup> have examined two such systems. Allyltrimethylgermane **13a** and allyltrimethylsilane **13b** gave 22% and 35% yields of the respective products **14**.



### 5.3.2. Unconjugated Aliphatic Dienes

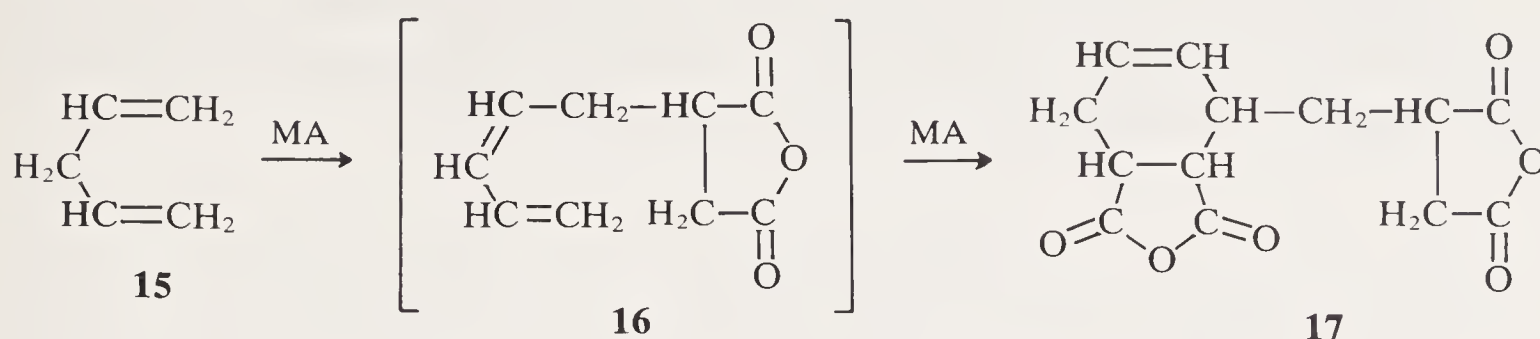
Open-chain unconjugated dienes may also be treated similarly. In systems where such unsaturation is far apart, the usual ene reaction may take place. When this is not the case, as for 1,4-pentadiene, the ene reaction would produce a conjugated diene which in turn could undergo a DA reaction. Alder and Munz<sup>(22)</sup> first studied this reaction by heating a benzene solution of the reactants for 60 h at 200°C and obtained an unexpected product with



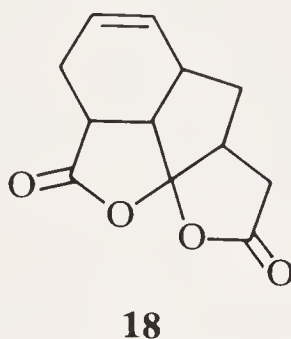
Table 5.2. Ene Reaction of MA with Unsaturated Esters

Olefin	Olefin/MA	Solvent	Temperature (°C)	Inhibitor	Time (h)	Yield (%)	References
Methyl undecylenate	1.0	Xylene	135–140	—	23	46	17
	1.0	—	215–230	—	2	58	17
	1.0	—	200	—	2	48	19
Methyl-hex-5-enoate	0.9	—	200	—	7–8	23	19
Methyl-but-3-enoate	1.0	—	200	—	7–8	~26	19
Methyl-crotonate	0.9	—	—	—	—	low	19
Methyl methacrylate	—	—	150	HQ	—	low	19
Methyl hex-3-enoate	—	—	210	—	9	low	19
Methyl oleate	—	—	215–230	—	—	40	17

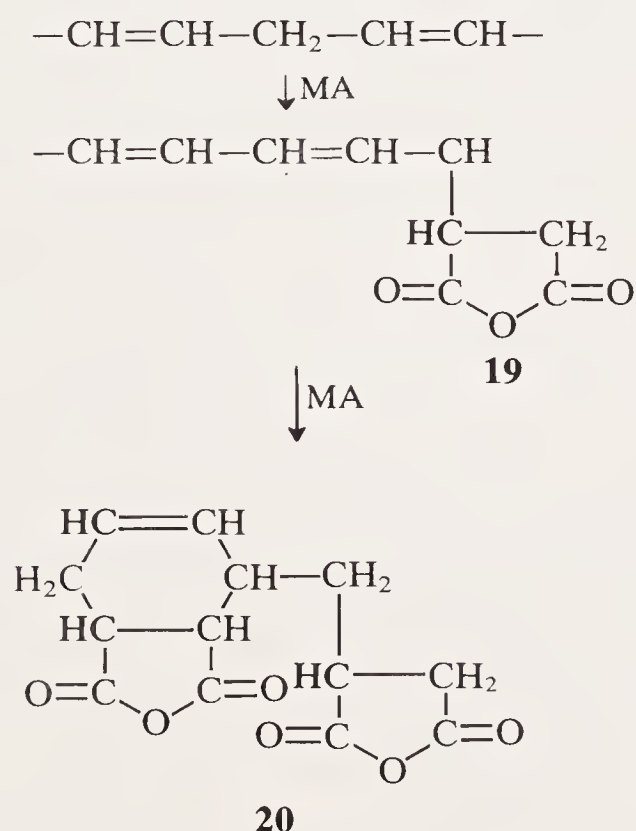
molecular formula  $C_{12}H_{12}O_4$ . However, under less-rigorous conditions ( $180^\circ C$  for 25 h) the expected product **17** was obtained.<sup>(23)</sup>



Hill and Barjer<sup>(24)</sup> reinvestigated the reaction with the help of NMR spectroscopy and studied the stereochemistry of the product. They proposed **18** as the structure for the unknown product obtained earlier by Alder and Munz.<sup>(22)</sup>



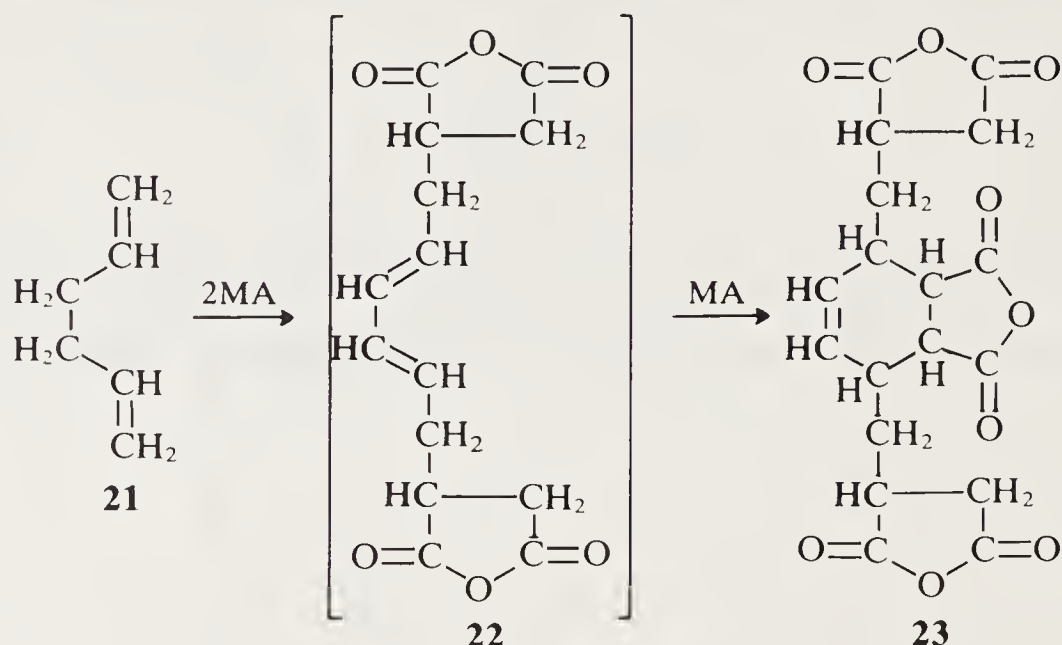
Naturally occurring linoleic acid contains a 1,4-diene. One might expect that the primary product from an ene reaction would lead to the conjugated diene **19** which could in turn undergo Diels–Alder reaction to give a product such as **20**.



A number of workers have studied this reaction in order to identify the products and understand its mechanism.<sup>(5,16,18,26–28)</sup> Rheineck and Khoe<sup>(18)</sup>

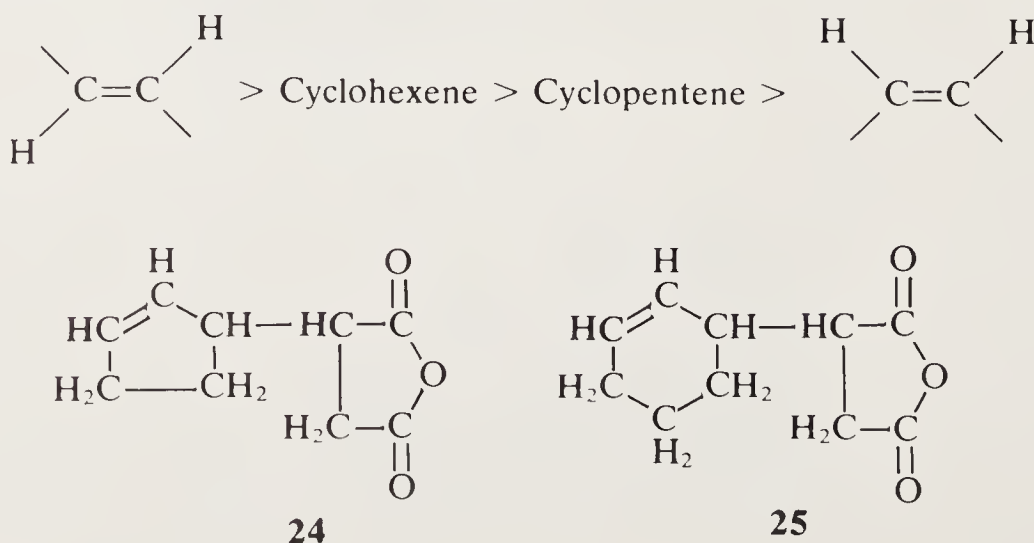
have isolated some of the products from a very complex reaction mixture. They suggest a radical mechanism to explain product formation.

Diallyl **21**, which is a 1,5-diene, gave the expected product from the ene reaction with 2 moles of MA to yield an intermediate conjugated diene **22** (not isolated). The latter gave a Diels–Alder adduct **23**.<sup>(23)</sup>



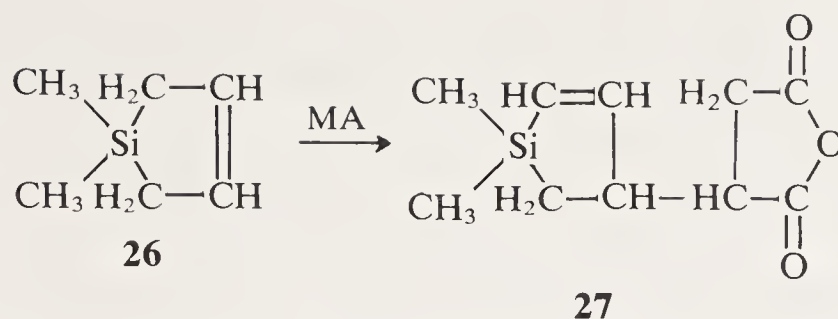
### 5.3.3. Alicyclic Olefins

Alder *et al.*<sup>(1)</sup> treated cyclopentene and cyclohexene with MA in benzene solution at 250°C. The products obtained were 2-cyclopentenylsuccinic anhydride **24** and 2-cyclohexenylsuccinic anhydride **25**. The inherent symmetry of starting olefins prevented the observation of the double-bond migration initially. Agami *et al.*<sup>(11)</sup> obtained only 3% yield of adduct **24** and 30% of **25** on heating a toluene solution of the reactants at 190°C for 24 h. The order of reactivity of alicyclic olefins as compared with aliphatic olefins is given below. Reactions of this type are not limited to carbocyclic compounds.

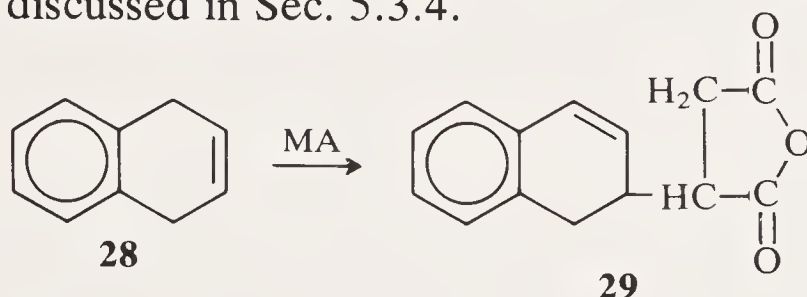


Laporterie *et al.*<sup>(21)</sup> obtained a 58% yield of product **27** from 1,1-dimethyl-1-silacyclopentene-3 **26** and MA at 150°C, thus suggesting the generality of the reactions. When the double bond in alicyclic olefins is not conjugated

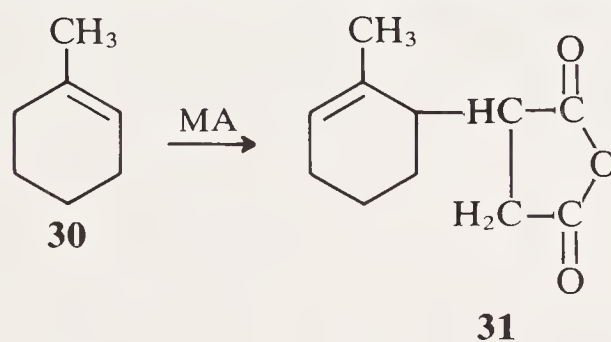




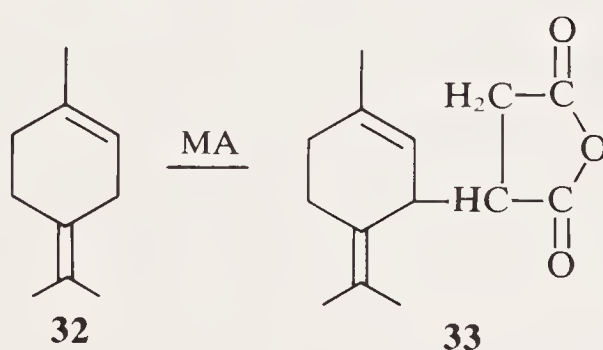
with a fused aromatic ring as in 1,4-dihydronaphthalene **28** the expected ene product **29** is obtained.<sup>(40)</sup> The cases of olefin bond in conjugation with the aromatic ring are discussed in Sec. 5.3.4.



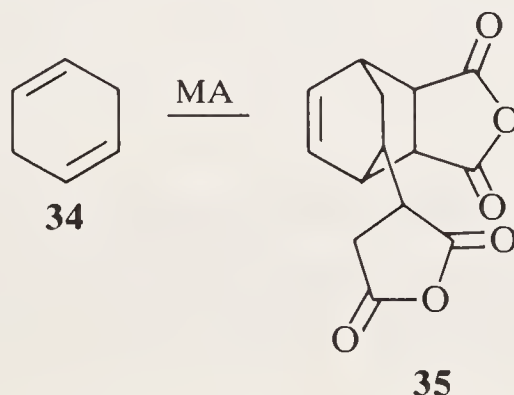
Alder and Dortmann<sup>(29)</sup> also reported the reaction of 1-methylcyclohexene **30** with MA and obtained a diastereomeric mixture of **31**. An



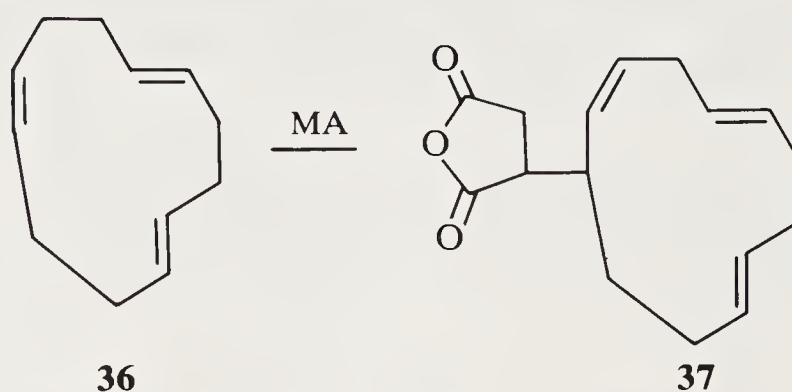
analogous natural product terpinolene **32** was studied by Hultzsch.<sup>(30)</sup> He assigned **33** as the structure of the product probably formed by a radical mechanism. (However, see pp. 158–159.)



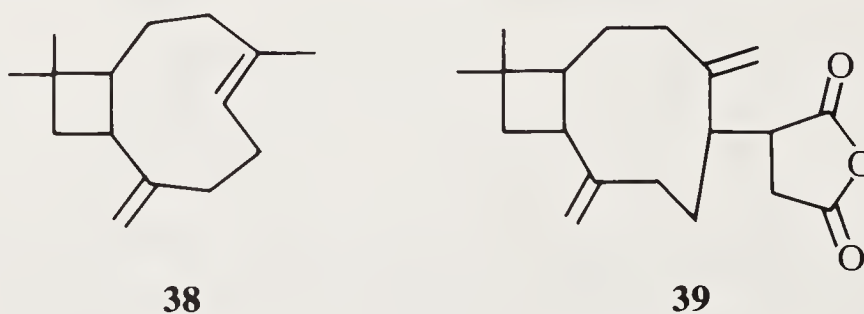
Alicyclic rings containing unconjugated diene and triene units have been examined. Alder and Munz<sup>(22)</sup> obtained the expected bis-MA adduct **35**, from 1,4-cyclohexadiene **34**.



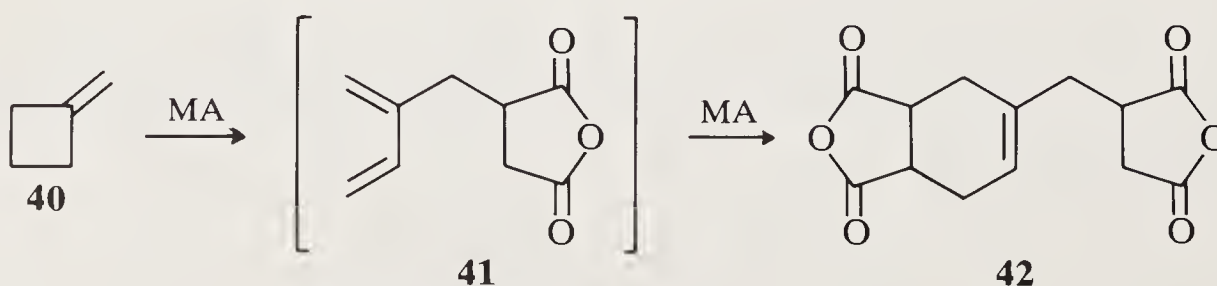
Stumpf *et al.*<sup>(92)</sup> reacted MA with *cis, trans, trans*-1,5,9-cyclododecatriene **36** in the presence of phenothiazine or thiamine as an inhibitor. The product *cis, trans, trans*-2,5,9-cyclododecatrienylsuccinic anhydride **37** was obtained in yields as high as 76%. MA could be substituted in this reaction with maleic acid, fumaric acid, or their esters. Wilke and Pfohl<sup>(93)</sup> had earlier incorrectly interpreted the adduct to be a Diels–Alder product when the reaction was allowed to run in the presence of 1–4 moles of MA at 180°C.



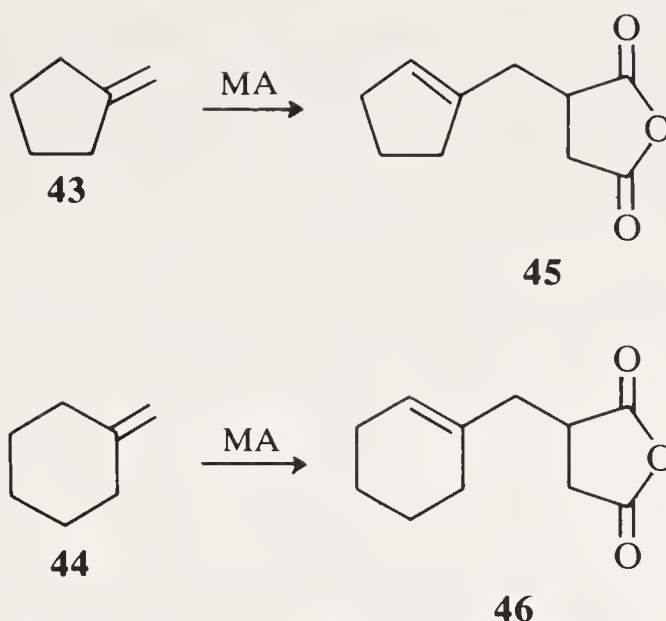
Caryophyllene **38**, a sesquiterpene, was studied by Alder *et al.*<sup>(1)</sup> However, the nature of the product was not readily apparent at the time. Nickon<sup>(35)</sup> later reexamined the reaction and assigned the following structure **39**. Note the migration of the internal olefin bond to the exocyclic position.



Alicyclic rings with exocyclic double bonds have been examined as well. Methylenecyclobutane **40** was reported by Alder and Dortmann<sup>(29)</sup> to yield a product containing two MA residues. Product **42** was rationalized to have been formed from initial ene reaction to give a diene intermediate **41**. The latter underwent Diels–Alder reaction with another mole of MA to yield the adduct **42** in 35% yield.<sup>(29)</sup>

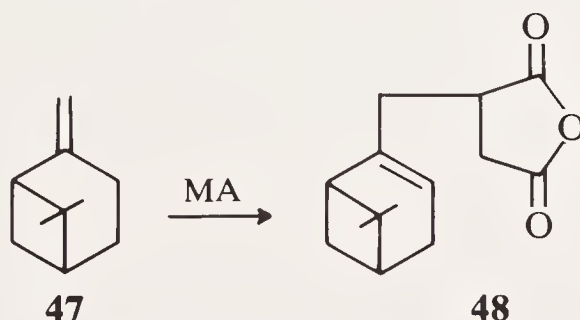


On the other hand, methylenecyclopentane **43** and methylenecyclohexane **44** undergo the ene reaction with a consequent migration of the double bond into the ring, giving products **45** and **46**, respectively.<sup>(36,37)</sup>



There is no systematic comparison of relative reactivities of internal versus external double bonds in the literature. As was evident in the case of caryophyllene **38**, where both of these entities were present, the result was that the internal double bond reacted. However, this may be a special case due to ring strain. Otherwise, in unstrained rings migration of the exocyclic double bond into the ring may be more common.

$\beta$ -Pinene **47**, a terpene hydrocarbon with exocyclic double bond, also undergoes the reaction.<sup>(38)</sup> Adduct **48** is obtained in a 31% yield on refluxing a xylene solution of the reactants for 20 h.<sup>(38)</sup>

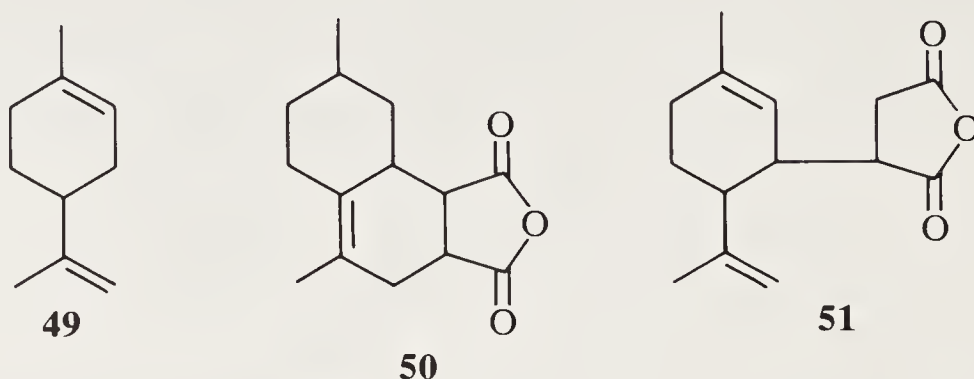


Recently, Gladysz and Yu<sup>(39)</sup> have utilized 40 kbars pressure at ambient temperatures to obtain a 74% yield of the adduct **48** in 17 h. This may be expected for reactions with high  $\Delta V^\ddagger$ . (See also DA reaction, Sections 4.5 and 4.8.) Asano and Le Noble<sup>(10)</sup> discuss activation and reaction volumes in solution and their effects on the DA reaction.

A word of caution may be necessary. One should be careful in interpreting the results of MA reaction with terpenes in particular, or in any system (i.e., the reactant and/or the product) that can undergo rearrangement under the reaction conditions. Alder and Schmitz,<sup>(31)</sup> for instance, observed that (+)-limonene **49** reacted with MA to yield **50**, a Diels–Alder product. Earlier, Hultsch<sup>(30)</sup> had reported the product to be **51**. Eschiazzi and Pines<sup>(32)</sup> had reported that limonene did not react with MA. The complexity of the system was studied in detail by Sugathan and Verghese.<sup>(33)</sup> They observed that (+)-limonene did not react with MA under mild conditions. At temperatures in excess of 75°C (or in acetone), various rearrangement products such as

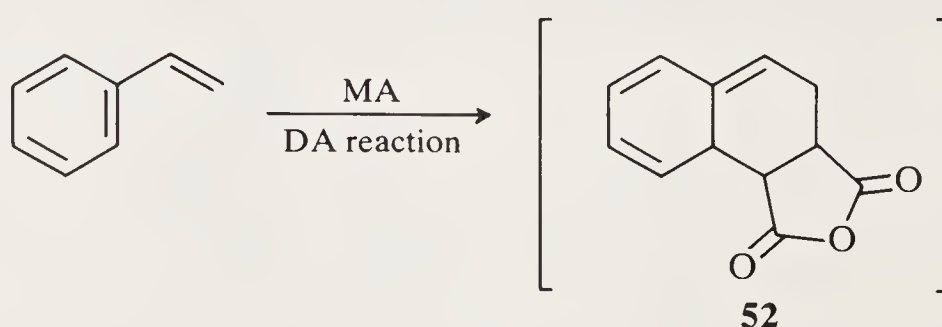


terpinolene,  $\alpha$ -terpinene, and its MA adduct and *p*-cymene were observed. Succinic anhydride (SA) was also observed as a product. The origin of SA was attributed to hydrogen transfer since aromatization to *p*-cymene was also observed. Similar results with  $\alpha$ -pinene and  $\beta$ -pinene were also reported.<sup>(34)</sup>

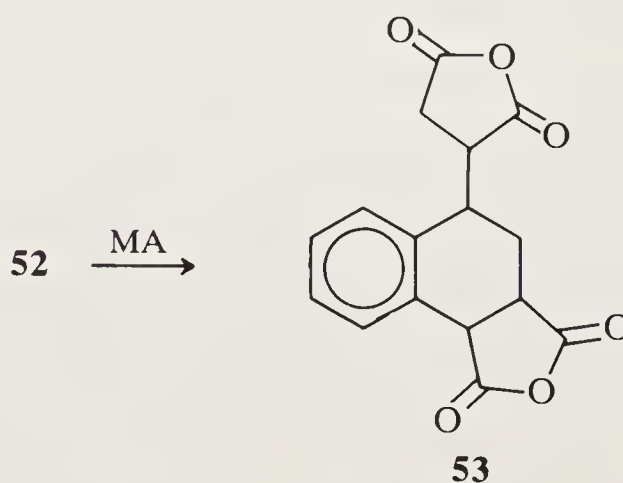


#### 5.3.4. Styrene Derivatives

As we saw in the Diels–Alder reaction, styrene derivatives could potentially undergo that reaction to yield **52**. The latter could enter into an ene reaction, a DA reaction, or aromatization. This has been a matter of controversy in the past which may be dispensed with here, since in specific cases as will be seen all possible alternatives are known. Given rearrangement,

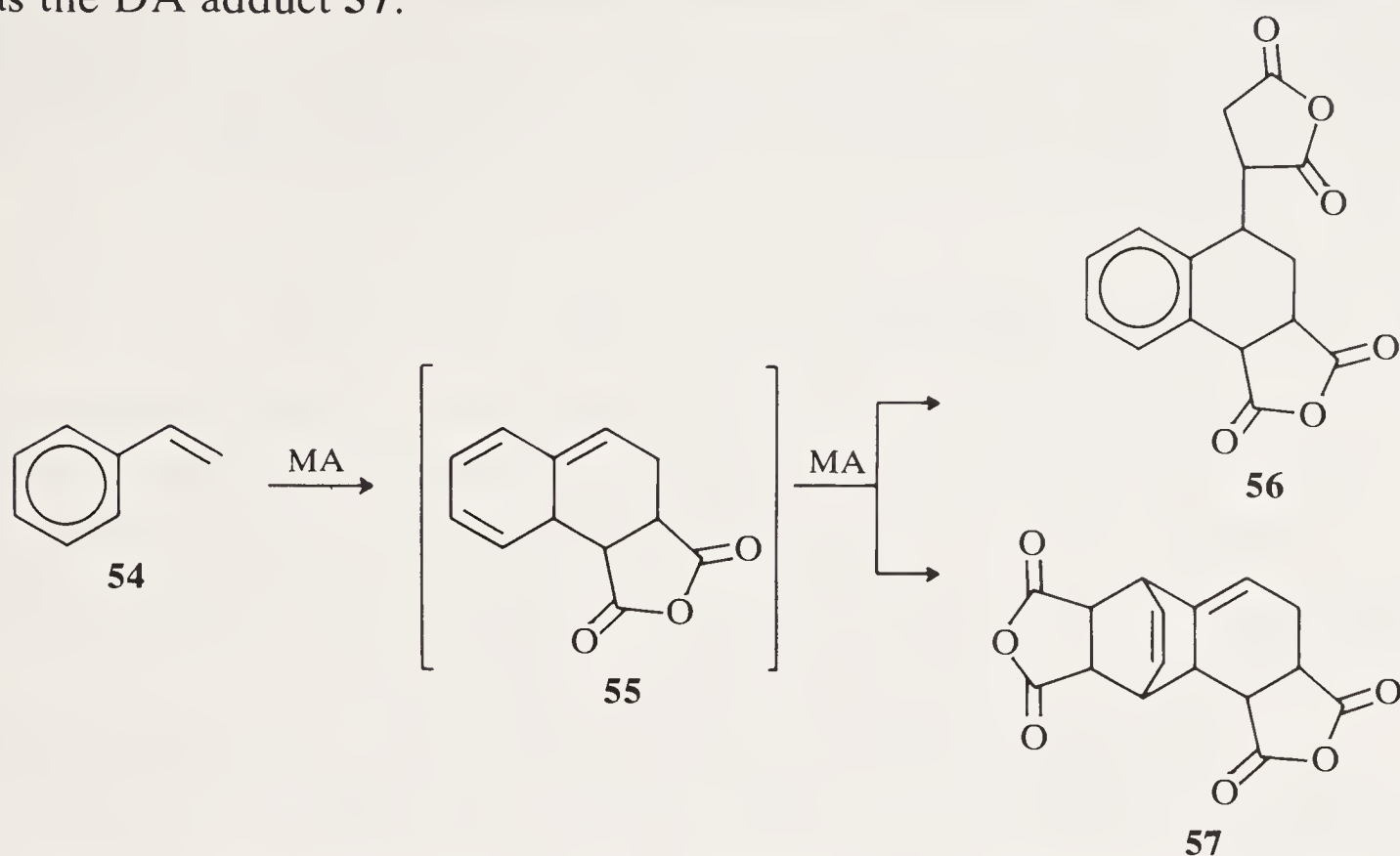


product **52** can aromatize as is known in the case of safrole, etc. However, the aromatization can also be brought about by the ene reaction with another molecule of MA. The product would then be a 1 : 2 styrene : MA adduct **53**.

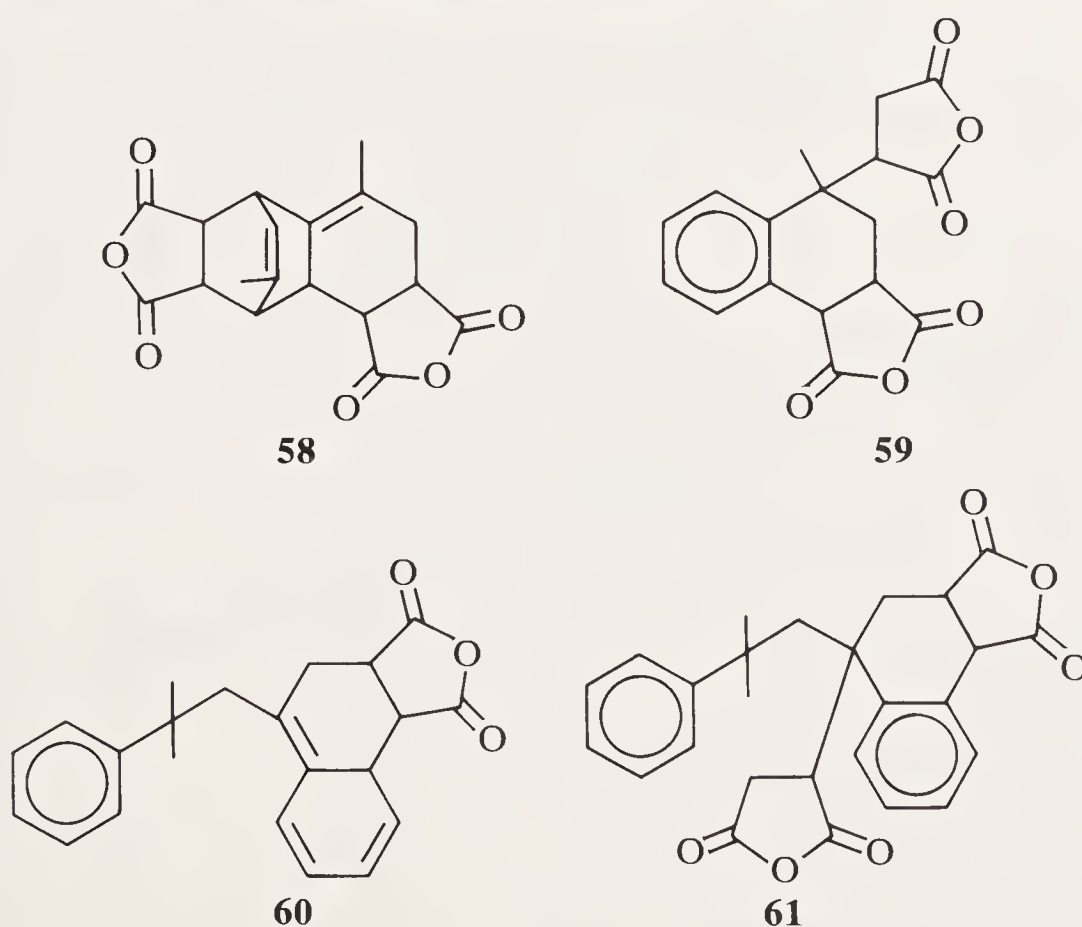


In part, that does happen, as Alder and coworkers<sup>(41)</sup> have shown in detail. Two 2 : 1 adducts in a ratio of 8 : 1 were isolated when using MA with styrene

**54.** The product from the ene reaction **56** of the intermediate **55** was the major product. Since the diene also forms as part of **55** the minor component was the DA adduct **57**.



Hukki<sup>(91)</sup> has studied the bis MA adduct of  $\alpha,p$ -dimethylstyrene. In a detailed study employing ozone cleavage, etc., it was shown that the adduct **58** was the result of two Diels-Alder reactions.



Zadra and Tazuma<sup>(42)</sup> have recently claimed surface-active compounds made from  $\alpha$ -methylstyrene and its dimer. The main products proposed are **59** from  $\alpha$ -methylstyrene and products **60** and **61** as mono and diadduct from

the dimer, respectively. Zadra and Tazuma<sup>(42)</sup> did not describe the use of any radical inhibitor in their example. However, the absence of a radical catalyst was claimed. Since a number of products form, it would be interesting to study if the ratios of the products are affected by the type of inhibitor used. Note that the structures proposed by Zadra and Tazuma are only suggestions for the main product. The dimer employed was a mixture as well.

#### 5.4. REACTION CONDITIONS AND THEIR EFFECTS

As is evident from Table 5.1, ene reactions are typically carried out at 140–250°C. In some cases, solvents such as benzene, toluene, and other aromatic solvents may be employed. For lower olefins, sealed systems are necessary. However, as we shall see later, for olefins such as polymeric olefins or methyl oleate, whose boiling points are sufficiently high, the reaction can be conveniently run in a flask under an inert atmosphere.

Since polymerization could be a possible side reaction, usually an inhibitor is incorporated. In two cases, a systematic study of the nature of the inhibitor has been made.<sup>(45,92)</sup>

Irvin and Selwitz<sup>(45)</sup> have studied the effect of the nature of inhibitor on the conversion of MA and the yield of the ene product. Their data are reported in Table 5.3. Note that each of the inhibitors increased the yield considerably.

Table 5.3. Effect of Inhibitors<sup>a</sup>

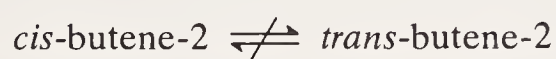
	Additive			
	None	2,2'-di( <i>p</i> -Hydroxy-phenyl) propane	Hydro-quinone	Pheno-thiazine
Amount of additive, gram	1	1	1	1
Temperature, °C	186–217	185–211	185–213	185–229
Time, hours	7	8	7	7
Weight in, grams:				
Dodecene-1	337	337	380	337
Maleic anhydride	98	98	115	98
Weight out, grams				
Dodecene-1	210	191	228	215
Maleic anhydride	10	22	17	35
Dodecenylsuccinic anhydride	163	180	220	173
Polymer	53	42	22	12
Conversion, wt. %				
based on maleic anhydride	90	78	85	64
Efficiency, % based on maleic anhydride	68	87	83	100

<sup>a</sup> From Reference 45.



As far as the fate of MA was concerned, phenothiazine was the best inhibitor reported, however, conversions were not complete. In each case, a polymer in varying amounts was observed but not characterized. (But see Benn *et al.*<sup>(47)</sup>) Very high conversions of MA would obviate the recovery and recycling of MA for commercial products. Dependence of the yield and tar generation on the nature of the inhibitor has also been reported by Stumpf *et al.*<sup>(92)</sup>

The yields can be significantly improved with lower olefins using toluene as a solvent and *t*-butylcatechol as the inhibitor.<sup>(8)</sup> It is also noteworthy that the reaction of butene-1 and MA gave a 9:1 mixture of isomers.<sup>(8)</sup> Berson *et al.*<sup>(14)</sup> have also examined *cis*- and *trans*-butene-2. Although these workers reported (see Table 5.1) lower yields it was found that the olefins did not interconvert during the reaction.



It may be remembered here that during the ene reaction, a new center of asymmetry is created and as a result, as in the other additions involving nonequivalent fragments, a mixture of diastereomers is formed.

The effect of reaction parameters on the yield of the adduct from oleic acid has been examined by Eslami.<sup>(20)</sup> Two isomers are obtained as expected—in yields as high as 80% in the presence of HCl or H<sub>3</sub>PO<sub>4</sub> as a catalyst. As shown in Fig. 5-1, in absence of the catalyst, yield of the adduct increased

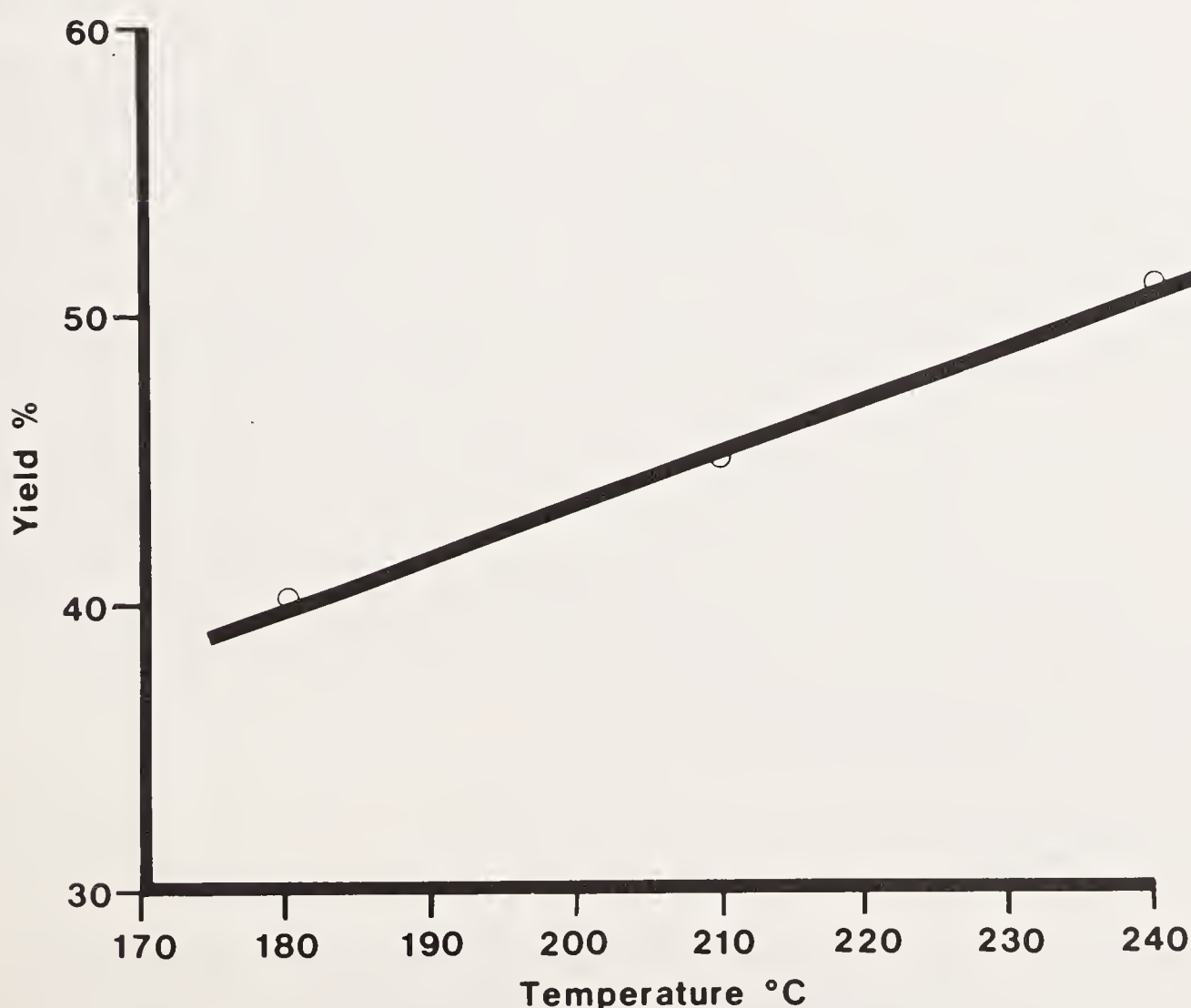


Fig. 5-1. Effect of temperature on yield: oleic acid + MA without catalyst. From Reference 20.

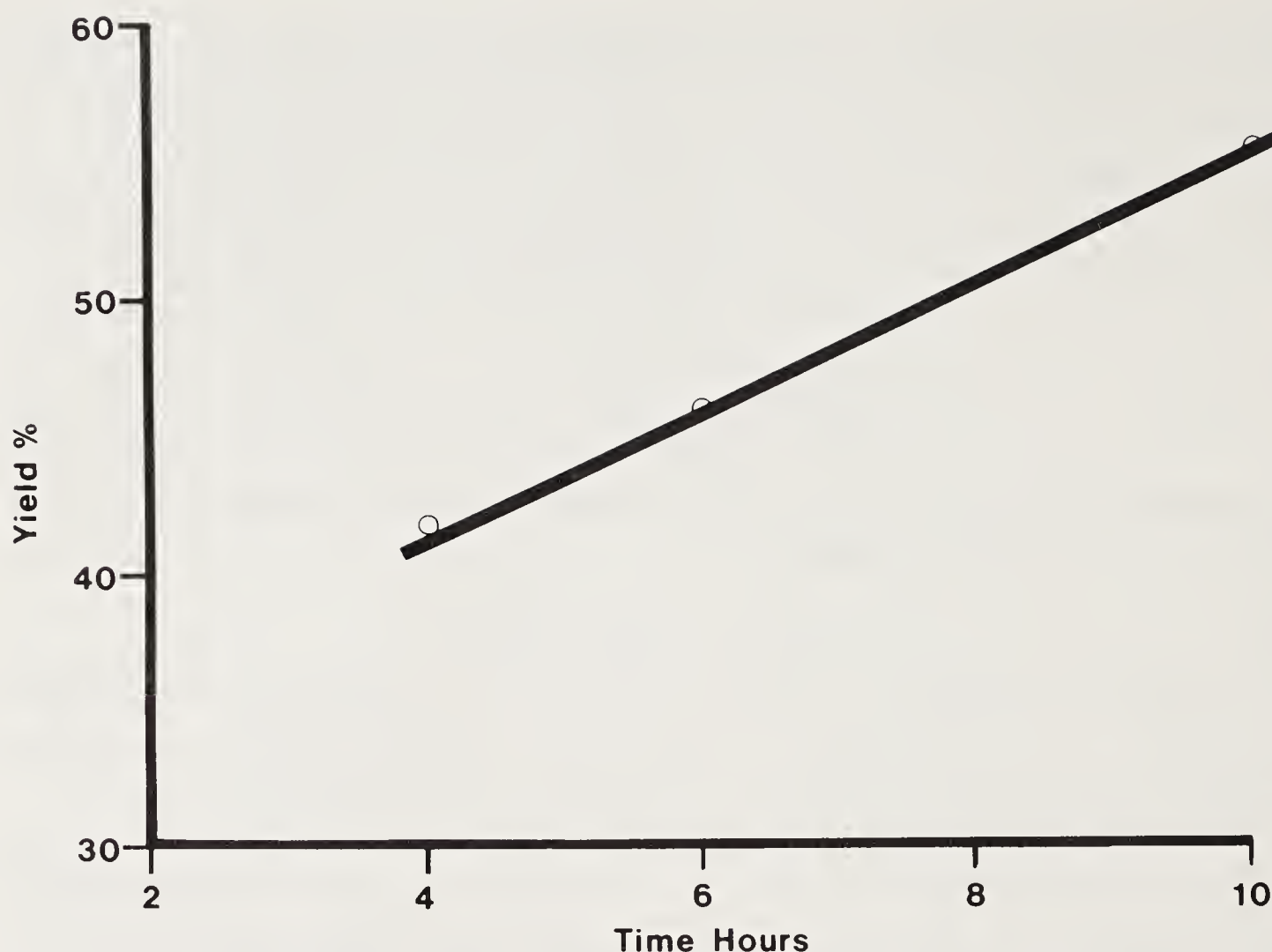


Fig. 5-2. Effect of reaction time on yield: oleic acid + MA at 200–210°C with no catalyst. From Reference 20.

with the reaction temperature in the range examined. The yield is also favorably affected by longer reaction time at a constant temperature of 200–210°C (Fig. 5-2). Although plots are nearly linear, no such trend outside the range is implied. Longer reaction times, however, may promote isomerizations and polymerization.<sup>(8)</sup>

Silverstone *et al.*<sup>(25)</sup> have examined the effect of temperature and the MA:olefin ratio using “methyl iso-oleate.” The latter was obtained by hydrogenation, dehydration, and splitting of castor oil and hence is a mixture. Their data are shown in Table 5.4. At higher iso-oleate content, the disappearance rate of MA is faster. Higher temperature also gives faster conversion of MA.

It probably is evident that this substitutive addition reaction of olefins with MA can be carried out using MA derivatives such as acids, esters,<sup>(90,92)</sup> imides, and so on. Choice of reagent is often governed by the nature and intended use of the products, yields, etc.

## 5.5. MECHANISM

It is difficult to view the ene mechanism strictly from the MA point of view since the understanding has developed from the study of MA as well as

Table 5.4. Reaction of Methyl Iso-Oleate with Maleic Anhydride<sup>a</sup>

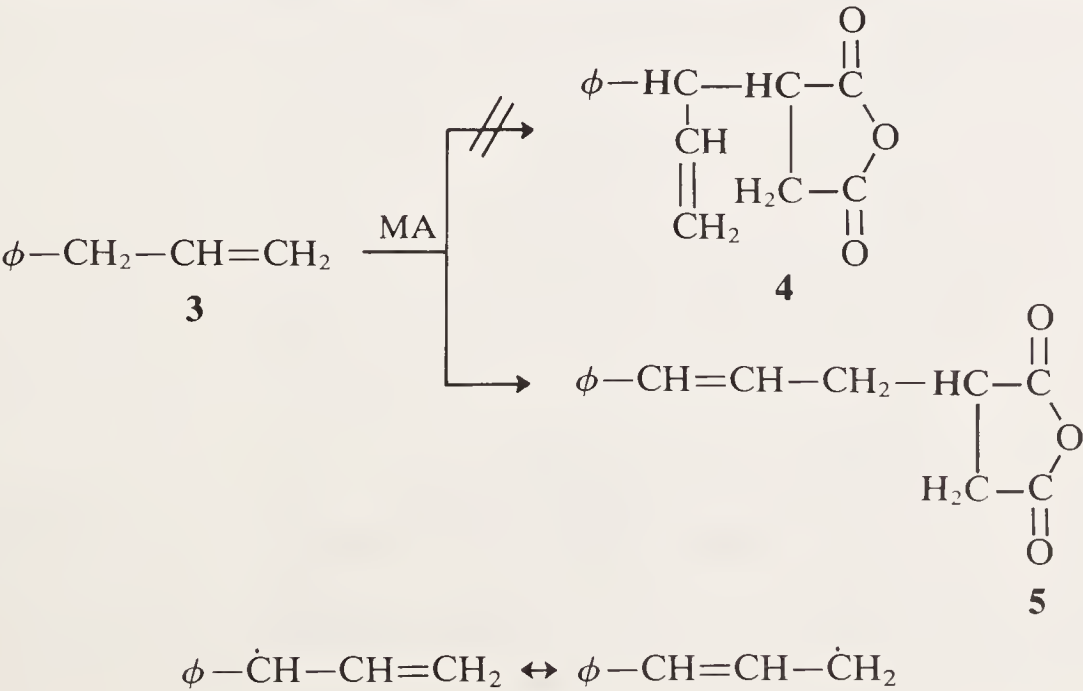
Molar ratio <sup>b</sup> MA : Iso-Oleate	Tempera- ture (°C)	Time (h)	MA disappeared (%)	Reaction <sup>c</sup> corrected (%)	Distillate (% MA)	Product weight (%)	Loss MA <sup>d</sup> (%)
0.5 : 1	200	5	82.2	69.3	2.1	38.4	12.9
0.5 : 1	220	5	95.2	(74.4)	0.4	38.8	20.6
1 : 1	200	5	68.8	55.6	14.1	47.8	13.2
1 : 1	220	5	85.5	67.6	7.4	66.4	15.9
1 : 1	180	5	40.3	37.9	17.7	28.8	10.9

<sup>a</sup> From Reference 25.  
<sup>b</sup> Each experiment used 400 g of ester and either 56.8 or 113.8 g of MA. (The fatty ester was thought to contain 85.5% iso-oleate, no correction having been made for the residual hydroxyl content of this estolide derived product.)  
<sup>c</sup> Corrected figures assume a steady loss of MA by sublimation, average hourly loss being the figure in the last column divided by 5.  
<sup>d</sup> This figure represents MA unaccounted for by analysis and assumed to be lost by sublimation.

other useful reagents such as formaldehyde, diethyl azodicarboxylate, selenium dioxide, and simple olefins, just to name a few. A number of mechanistic and labeling studies employing MA as a reagent has shed considerable light on the mechanism. In this section, therefore, we will limit the discussion to mechanisms as studied with MA, and, where applicable, highlight the studies with other reagents.

5.5.1. Labeled Olefins

The results of the reactions of various olefins with MA had been, in the past, interpreted as initiated by a radical<sup>(5)</sup> or a polar process<sup>(1)</sup> involving dissociation of allylic hydrogen. It was soon recognized, as shown earlier, that since cinnamylsuccinic anhydride **5** was the only isolable product obtained







that propene-1-<sup>14</sup>C did not isomerize under the conditions of the reaction. The retention of the label in **64** suggests:

- The double bond does migrate as a consequence of the reaction.
- No long-lived radical or charged allyl species is formed, since that would lead to mesomeric species leading to scrambling of the label.

5.5.2. Kinetic Studies

The majority of the work involving the reaction of MA with olefins is qualitative in nature. Reactivities have generally been concluded on the basis of yields. At the same time, some effort has been spent to understand the kinetics. Rondesvedt and Wark<sup>(44)</sup> examined the reaction of allylbenzene **3** with MA and observed the reaction to be second order overall, first order in each component. Recently Benn and coworkers<sup>(47)</sup> have reached similar conclusions from the kinetic investigation of a number of olefins with MA. The rates were computed three ways, i.e., from the rate of disappearance of the individual reactants and appearance of the product by GLC analysis. Mass balances by this method were claimed to be 98%. Their rate data are shown in Table 5.5. Based on their rate studies and additional work, the following

Table 5.5. Kinetics of MA Reaction with Olefins<sup>a</sup>

Alkene	Temperature (°K)	Rate constant, 10 <sup>7</sup> × <i>k</i> (kg <sup>-1</sup> s <sup>-1</sup> )		
		From maleic anhydride	From alkene	From product
Hex-1-ene	398	3.721	4.051	4.140
	448	91.30	97.21	90.73
Isohexene	398	4.146	3.995	3.964
Oct-1-ene	398	3.746	4.023	3.399
	421	21.80	21.92	22.18
	448	96.41	93.92	90.15
Dodec-1-ene	398	4.140	4.300	4.019
	448	101.3	93.06	80.61
	447	364.9	407.8	287.3
	497	831.7	954.9	753.8
<i>cis</i> -Dec-5-ene	411	6.786	6.053	6.628
	433	18.04	18.24	17.99
	455	53.08	56.88	57.25
<i>trans</i> -Dec-5-ene	411	18.11	17.35	18.13
	433	49.46	54.61	50.95
	455	162.4	151.8	169.3

<sup>a</sup> From Reference 47.

observations on the overall second-order processes were made:

- The presence of a free-radical inhibitor (Quinol) had no effect on the reaction rate. In the absence of an inhibitor, a side reaction leading to copolymer formations occurred. Thus, a free-radical chain process for the ene reaction was ruled out.
- *o*-Dichlorobenzene, nitrobenzene, and oct-2-enylsuccinic anhydride were employed as solvents. The rates were not affected by a change of solvents. Similar observations have also been made in the reaction of diethyl azodicarboxylate with 1,3-diarylpropene.<sup>(48)</sup> Thus, a discrete ionic species may be ruled out as an intermediate. Little or no solvent effects are anticipated in “no mechanism” reactions.<sup>(49)</sup> The lack of a solvent effect does not rule out some charge transfer in the transition state leading to a short-lived zwitterion.
- The length of alkyl chain on the olefin had little effect on the rates, suggesting that the alkyl substituent orients itself away from MA in the transition state. Similar observations have been made by Friedrich *et al.*<sup>(50)</sup> during the study of the MA reaction with 2,3,3-trimethylbutene-1.

### 5.5.3. Activation Parameters

Rondestvedt and Wark<sup>(44)</sup> studied the effect of temperature on the rate of the ene reaction of MA with **3**. Activation energy was determined to be 20 kcal/mole in the temperature range 127–153°C. Benn *et al.*<sup>(47)</sup> have employed a much wider temperature range, 125–224°C. Data in Table 5.6 show the activation energy to be in the same general range as found by Rondestvedt and Wark.<sup>(44)</sup> Note that the ene reaction has higher activation energy than the DA reaction. Thus ene reaction occurs at higher temperatures complicating mechanistic studies.<sup>(103)</sup>

Entropy of activation is a more conclusive parameter in this case. Large negative entropy suggests a highly organized transition state. The values are similar to the concerted Diels–Alder reaction. Thus, based on kinetic and

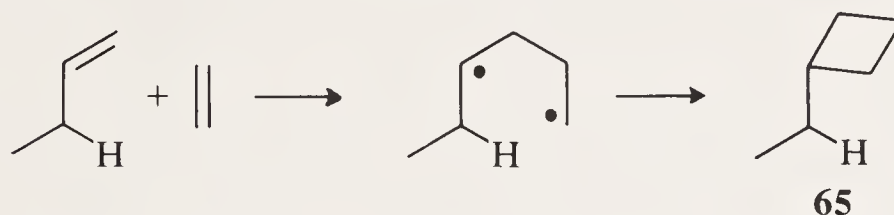
Table 5.6. Kinetic Parameters for MA Reaction with Olefins<sup>a</sup>

Alkenes	Energy of activation (kcal/mole)	Entropy of activation (cal/deg mol)
Alk-1-enes	21.5 ± 0.7	−30.3 ± 1.05
<i>cis</i> -Dec-5-ene	18.5 ± 1.5	−45.6 ± 3.53
<i>trans</i> -Dec-5-ene	18.4 ± 1.5	−42.5 ± 3.53

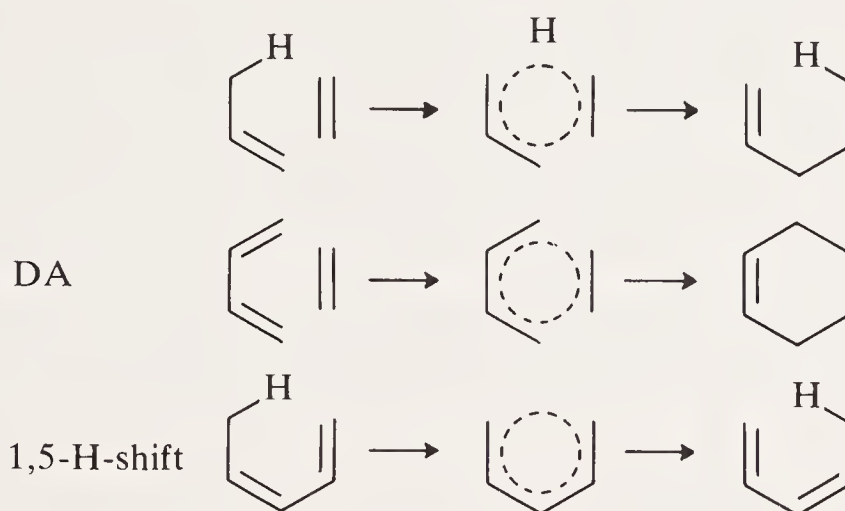
<sup>a</sup> From Reference 47.



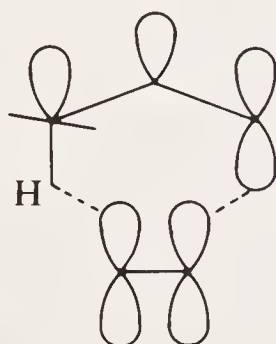
activation data, it seems that the reaction may proceed by a concerted process. However, a biradical mechanism cannot be ruled out. Bartlett<sup>(51)</sup> has suggested that a biradical intermediate, if formed, may be converted to a cyclobutane derivative **65** at least partially. In the absence of any cyclobutane formation, one may say that the ene reaction follows a concerted course.



These conclusions are similar to those reached earlier on the ene reaction in general. It is generally recognized that the reaction is related to the Diels–Alder reaction and can be considered to be an intermolecular analogue of the symmetry-allowed 1,5-hydrogen shift.<sup>(6,52)</sup>



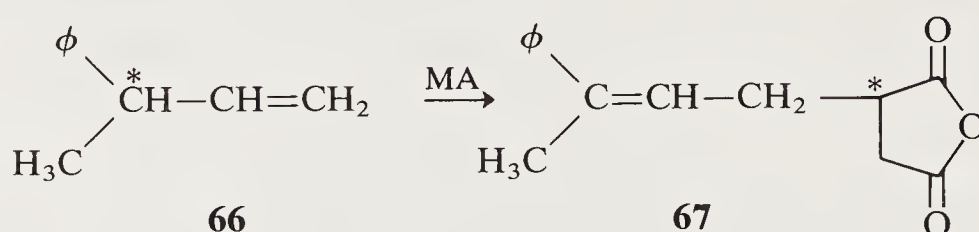
It may be recognized that the bonding in the transition state may be maximized differently for each reaction: For the concerted ene reaction, allylic resonance and hence the stabilization is maximized by turning the axis of the C—H bond undergoing breakage parallel to the *p* orbital of the double bond.<sup>(6)</sup>



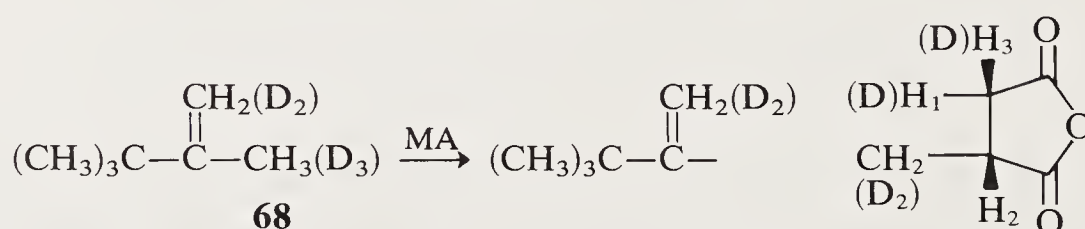
#### 5.5.4. Stereochemistry

As we have seen, high entropy of activation suggests a highly organized transition state. That being the case, the relative bulk of the substituents may play a decided role in determining the exact geometry of the transition state. This has been observed in part by Hill and Rabinovitz<sup>(53)</sup> who obtained an

optically active product from optically active olefin and MA. Thus, heating a solution of (R)(-)-3-phenyl-1-butene **66** ( $[\alpha]_D = -68^\circ$ ) and MA in *o*-dichlorobenzene for 12 h at  $210^\circ\text{C}$  gave (3-phenylbuten-2-yl)succinic anhydride **67** ( $[\alpha]_D = -145^\circ$ ). Although the optical activity was imparted to the product, the degree of optical purity was not determined.

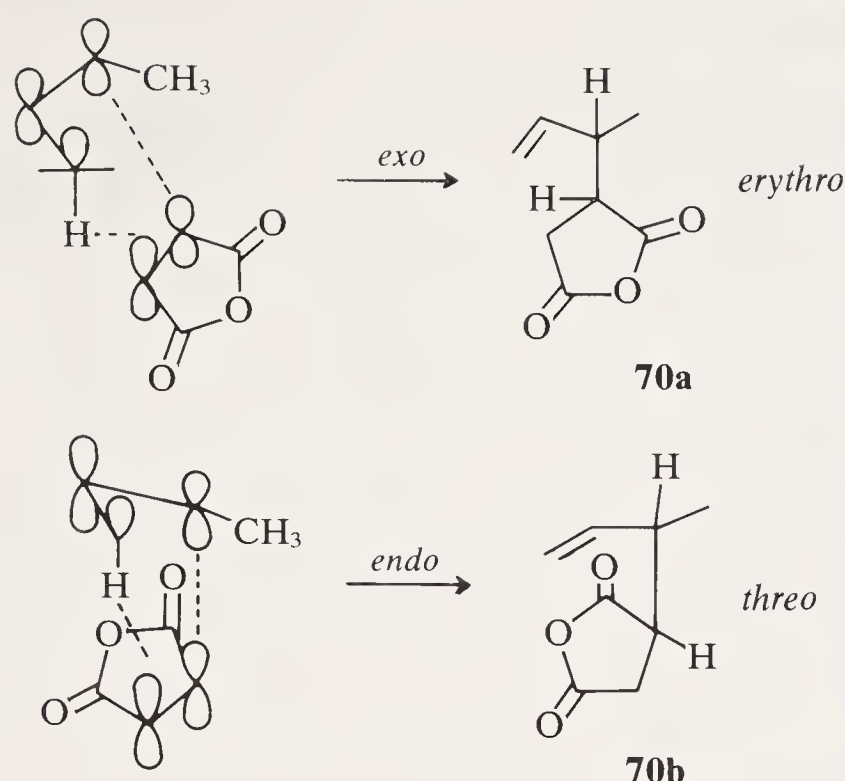


In a concerted process, an olefin can add *cis* or *trans* to MA. These are represented as *syn-syn* and *anti-anti* concerted processes and are symmetry allowed.<sup>(6)</sup> We have seen that the predominant product obtained is a *trans*-olefin<sup>(47)</sup>; however, thermodynamic stabilities of the products cannot be ruled out as a contributing factor. To eliminate this stability bias, Friedrich *et al.*<sup>(50)</sup> have investigated the reaction of 2,3,3-trimethyl-1-butene **68** and its deuterated analogue. From the NMR of the product, it was concluded that starting with deuterated olefin, H<sub>2</sub> and H<sub>3</sub> (i.e., those originating from MA) were *cis*. Since the limit of detectability of the other isomer is 30%, it may be concluded that the ene reaction is at least 70% *cis*-stereospecific.

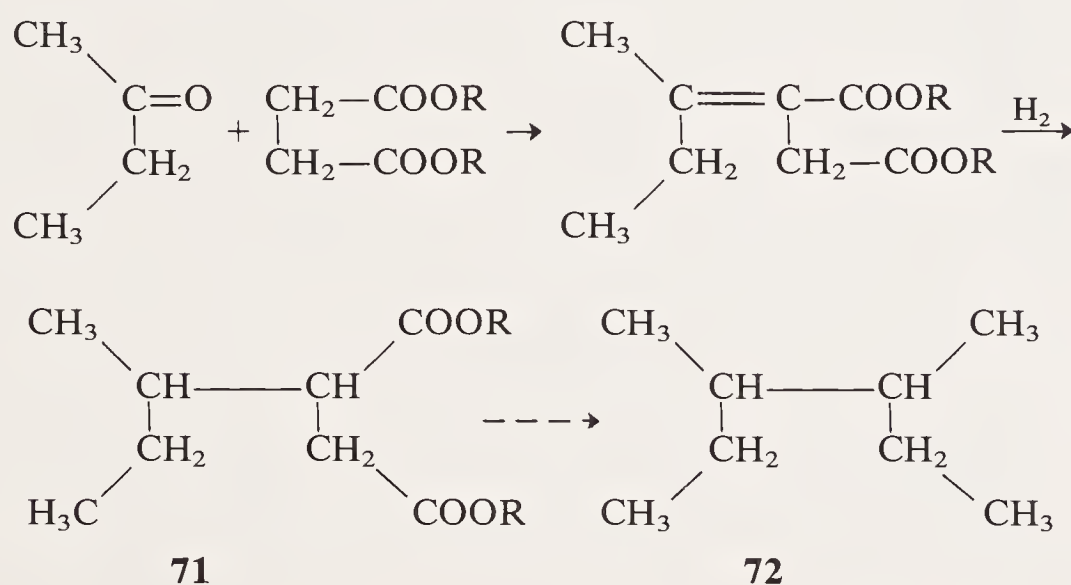


#### 5.5.5. *Endo* versus *Exo* Geometry

In the Diels–Alder reaction, unlike in the ene reaction, a product with a six-membered ring is formed. By the determination of the product geometry therefore, a conclusion may be made about the *exo* versus *endo* stereoselectivity of the DA reaction. In the ene reaction, given a concerted process, the six-membered ring exists in the transition state only. However, the *endo* versus *exo* preference in the transition state can be determined from whether the *threo* or the *erythro* diastereomer is preferred in the product. Berson *et al.*<sup>(14)</sup> have examined the ene reaction of *cis*- and *trans*-2-butenes. From *cis*-2-butene a 20–30% yield of the product diastereomers was obtained. The distribution for **70a** was 15–20% and for **70b** 80–85% was observed. The product ratio was kinetically controlled since the same ratio was observed at lower conversion. The isomeric *trans*-2-butene gave **70a** 57% to **70b** 45%. The configurational assignment was made by converting the diastereomers to



the hydrogenated ester derivative and also by an independent synthesis of the hydrogenated ester derivative **71** by Stobbe condensation and hydrogenation followed by resolution, as shown below.



Alternatively, in a series of steps, including resolution **70a** and **70b** were converted to 3,4-dimethylhexane **72**. Optically active **72** was obtained from **70b** and the *meso* form of the hydrocarbon was obtained from **70a**. Thus it appears that qualitative preference for *endo* addition is observed.

Benn *et al.*<sup>(47)</sup> argue, on the other hand, that steric hindrance plays a major role in determining whether the *exo* or *endo* transition state is traversed. For instance, in the case of  $\alpha$ -olefins and *trans*-olefins, in order to achieve a transition state leading to a product with a *trans* double bond, *exo* addition should be favored based on examination of molecular models. Their explanation for  $\alpha$ -olefins is represented in Figs. 5-3 and 5-4.

With *cis*-5-decene, the *exo* transition state is sterically hindered as represented in Fig. 5-4. In the activation data in Table 5.6 *cis*-5-decene does have slightly higher entropy of activation than *trans*-5-decene. However, the



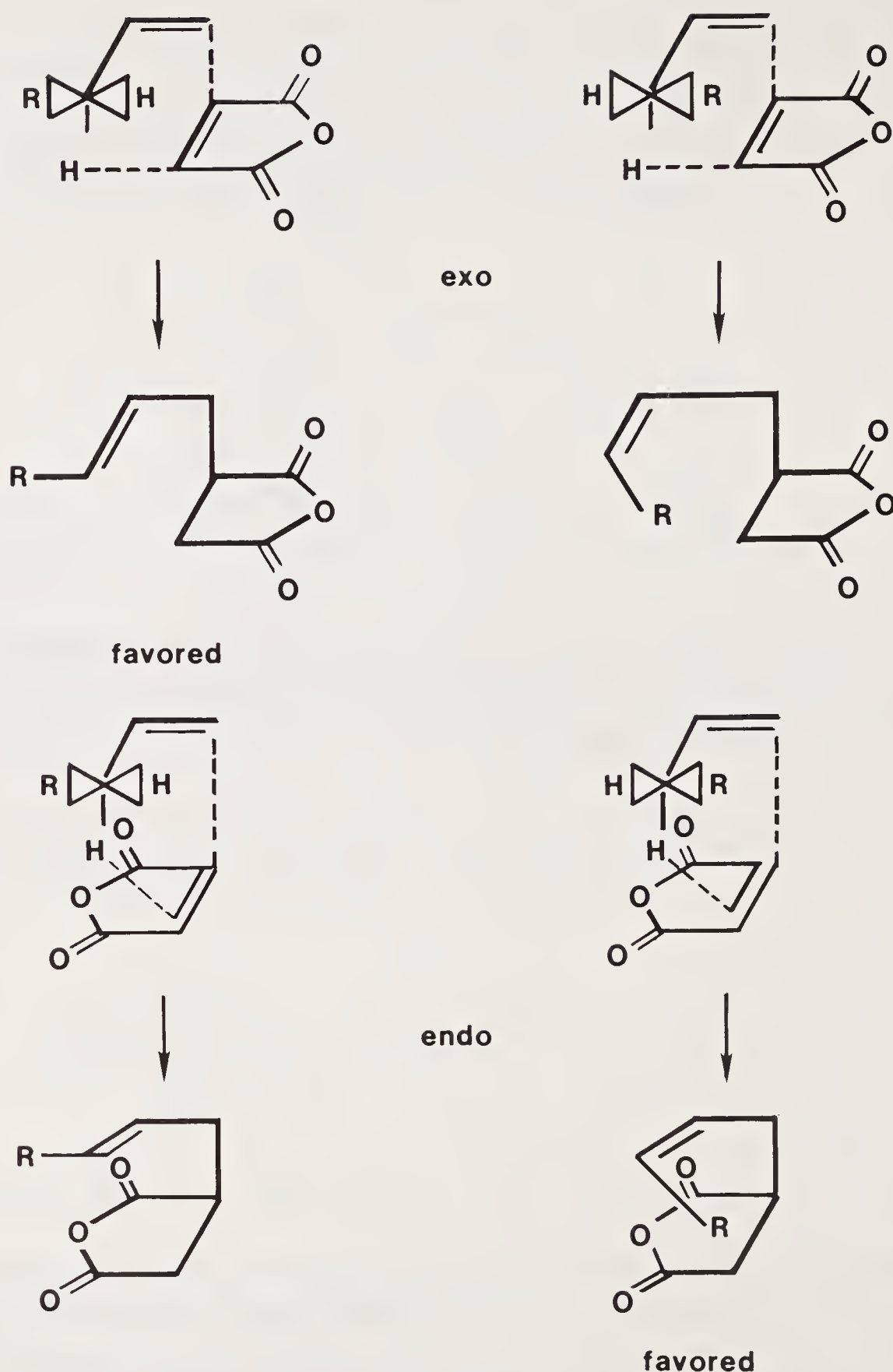


Fig. 5-3. Stereochemistry of ene reaction:  $\alpha$ -olefin with MA. From Reference 47.

selectivity in each case as shown by Berson *et al.*<sup>(14)</sup> is not clear-cut. Further work in this area of stereochemistry is needed before the question of stereochemical selectivity can be resolved.

#### 5.5.6. The Timing of Bond Formation

Since a cyclic transition state is suggested in a concerted process, it is natural to ask to what extent is the C—C bond formed and the C—H bond

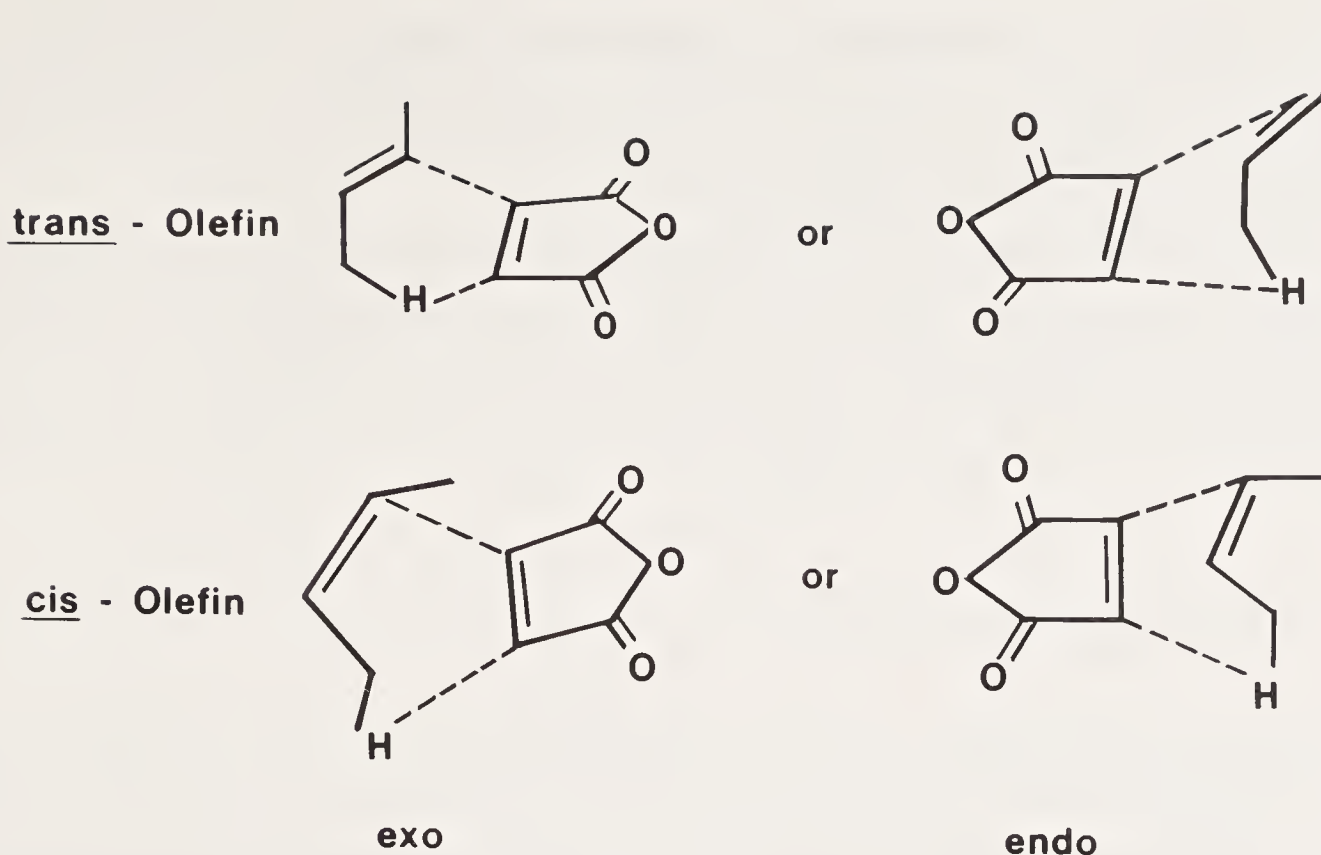
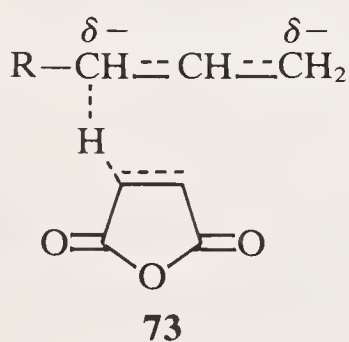


Fig. 5-4. Stereochemistry of ene reaction *cis*- and *trans*-olefin with MA. From Reference 47.

broken in the transition state? In general, this is a difficult question to answer. Since there are a number of ene reagents, one may derive information from these other systems. However, caution should be exercised. For example, for a concerted ene process, the transition state forms so as to maximize allylic resonance. This can be adequately achieved with simple olefins. However, with cyclopentene and cyclohexene and related systems, such a transition state would be difficult to achieve due to the rigidity of the molecule. Note that cyclopentene was reported to yield only 3% of the adduct.<sup>(11)</sup>

Often kinetic isotope effects ( $k_H/k_D$ ) are useful measures of the extent of bond formations in the transition states. Here again the data available are from other enophiles. A broad spectrum of behavior is obtained<sup>(6)</sup> making generalizations difficult.

Agami *et al.*<sup>(54)</sup> have studied the reactivity of various olefins with MA<sup>(11)</sup> as well as other enophiles such as acrylonitrile<sup>(54)</sup> and formaldehyde.<sup>(55)</sup> They suggest that the sequence of reactivity parallels that observed in the ethylation of sodium alkyls.<sup>(56,57)</sup> Since a carbanion is involved in the latter case, Agami *et al.*<sup>(11)</sup> proposed that attack by the enophile occurs on the hydrogen alpha to the double bond giving rise to a pseudocarbanionic complex **73**. This

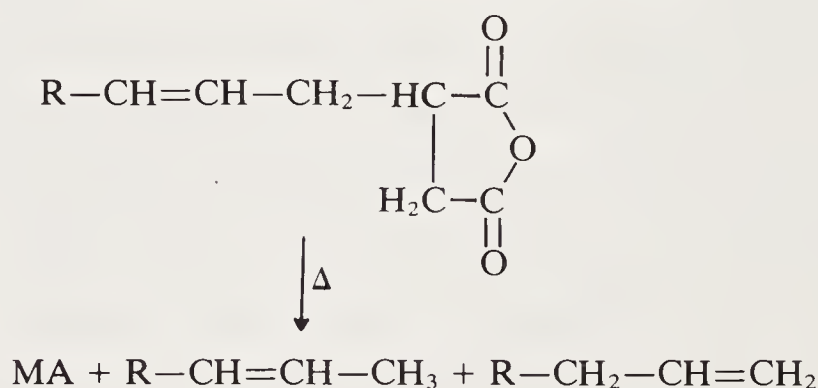


requires that the C—H bond be considerably broken in the transition state. However, it may be remembered that a C—H bond is energetically very costly<sup>(58)</sup> and Hoffman<sup>(6)</sup> suggests that making of the C—C bond may be in the lead as a more reasonable alternative.

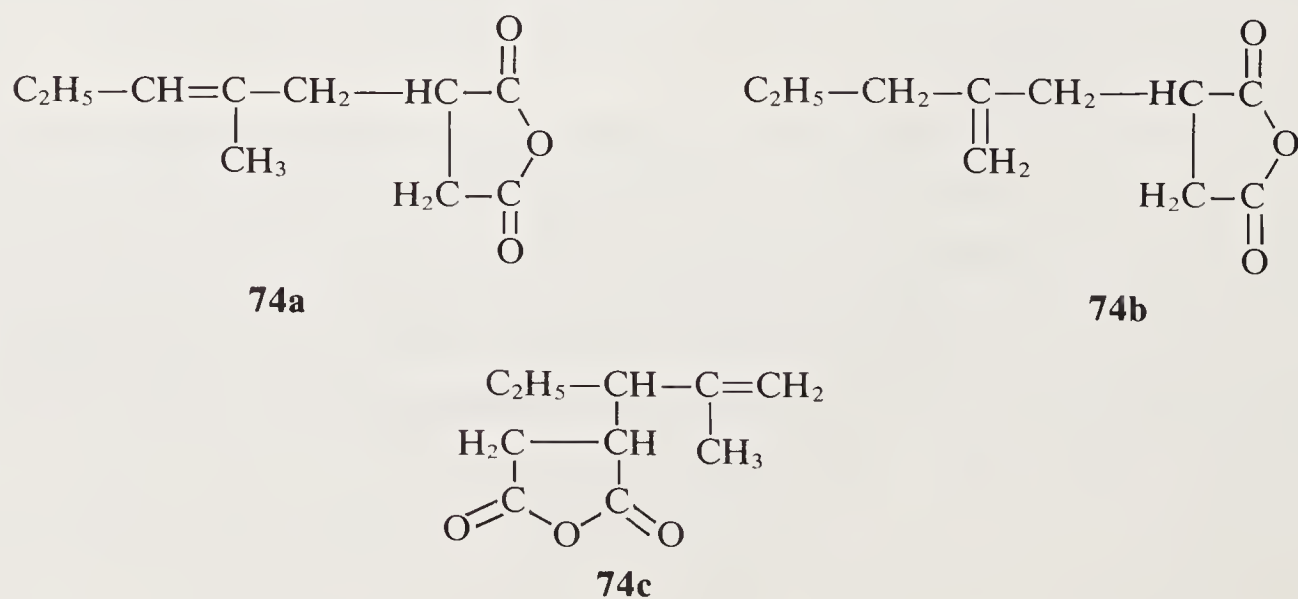
In conclusion, therefore, it is difficult to decide whether the ene reaction follows a concerted stepwise or an in-between route. Depending on the nature of olefin and enophile, all are possibilities. It may be that where an optimum geometry for a preferred transition state can be achieved, a concerted process is favored.

## 5.6. RETROENE REACTION

As in the Diels–Alder reaction where the retroprocess contributed to the understanding of the reaction, attempts have been made to use the retroene to this advantage. Agami *et al.*<sup>(11)</sup> have observed that the retroene process does not necessarily produce the same starting olefin.



When running the condensation starting with 2-methyl-pentene-1 and MA, they observed that a mixture of anhydrides **74a**, **74b**, and **74c** was formed.



In a kinetically controlled process at 140°C for 5 h only **74a** and **74b** are formed in a ratio of 73:27. Similar ratios have been observed with other ene reagents, e.g., formaldehyde<sup>(55)</sup> and acrylonitrile.<sup>(54)</sup> However, heating at



Table 5.7. Effect of Temperature on Unreacted Olefin in the Reaction MA + 2-Methylpentene-1<sup>a</sup>

Temperature (°C)	Time (h)	Anhydride yield (%)	% 2-Methyl- pentene-2
125	48	35	26
160	5	9	4
160	25	45	21
160	72	56	66
160	96	64	73

<sup>a</sup> From Reference 11.

160°C for 96 h produced an equilibrium mixture of anhydrides containing 60% **74a**, 8% **74b**, and 21% **74c**. The olefin removed from the mixture also seemed to contain an equilibrium mixture of 2-methylpentene-1 (27%) and 2-methylpentene-2 (73%). The effect of temperature on the unreacted olefin composition is shown in Table 5.7. It may be noted that in the absence of MA but using succinic anhydride, only 7% of the isomerized 2-methylpentene-1 was obtained. Thus, direct thermal isomerization of olefin plays an insignificant role.

The above suggests that the mixture of olefins obtained during the reaction results from decomposition of the alkenylsuccinic anhydride product. However, since a mixture of starting olefin is obtained, it can not be truly classified as a retroreaction. Agami *et al.*<sup>(59)</sup> proposed a mesomeric carbanion participating in the degradation reaction. The conclusions were based on the analogy of base-catalyzed decomposition of hydroxymethyl derivatives.<sup>(55)</sup> It was suggested that the degradation reaction is in equilibrium with the ene reaction leading to condensation. However, generalized conclusions may be premature.

5.7. CATALYSIS

In general, the catalysis aspects of the ene reaction of MA with olefins remains superficially explored. Homogeneous or heterogeneous Lewis and Bronsted acids are potential catalysts for the process and their sysematic study may shed some further light on the mechanism of the process while helping the commercial utility of products by enhancing yields and rates.<sup>(6)</sup> Based on the analogy of the DA reaction, it is possible that catalysis by Lewis and Bronsted acids is due to complexation of the catalyst with the anhydride function. A recent review of Lewis acid catalysis of the ene reaction discusses related aspects.<sup>(103)</sup>

Eslami<sup>(20)</sup> studied the reaction of oleic acid with MA. A maximum yield (80%) of a mixture of isomers was obtained when hydrochloric acid or phosphoric acid was employed as a catalyst. Phosphonic and phosphinic acids have also been claimed.<sup>(71)</sup> Alkyl chlorides have been used as starting material.<sup>(60)</sup> One may assume that olefin forms as an intermediate, however, the effect of generated HCl on the reaction is not clear.

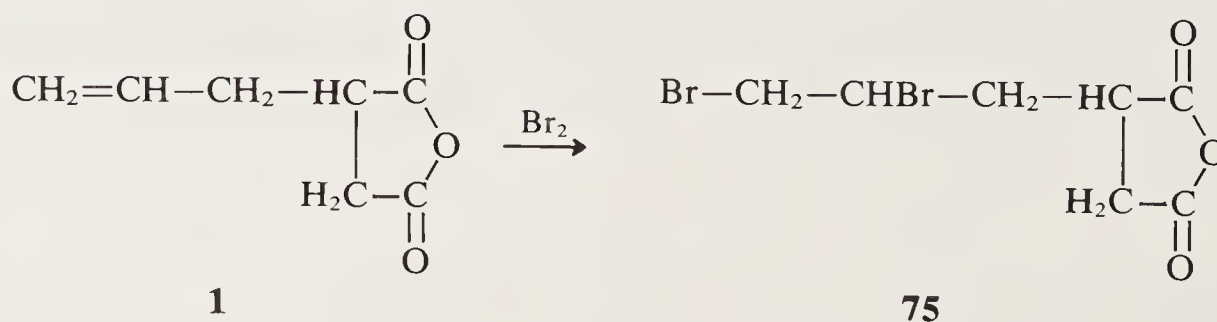
In a recent Japanese patent<sup>(61)</sup> a flow reaction has been described on a zeolite-based catalyst. Shorter contact times and lower temperatures are claimed with unsaturated fatty acid and ester.

Cohen<sup>(62)</sup> obtained an alkenylation product in a stagewise addition of anhydride and Cl<sub>2</sub> catalyst, with polybutene as starting olefin. Since this effort was product related, no conclusions can be derived on the role of radicals in the process, since chlorine can give rise to a chain process.<sup>(63)</sup> Use of Br<sub>2</sub> and HBr have also been reported.<sup>(99)</sup>

## 5.8. APPLICATIONS

The synthetic utility of the ene reaction of MA (and other enophiles) is well demonstrated. The products being unsaturated anhydrides, offer a potential as a monomer or as an intermediate.

Addition of bromine to allylsuccinic anhydride **1** gives rise to the dibromo derivative **75**. Inclusion of such material in polyesters has been claimed to improve fire retardancy of the product. The resin made with **75** was described as having self-extinguishing properties.<sup>(7,64-66)</sup> Bis-(2-hydroxyalkyl)-esters of **75** has been converted to flame-retardant urethanes.<sup>(67,68)</sup>

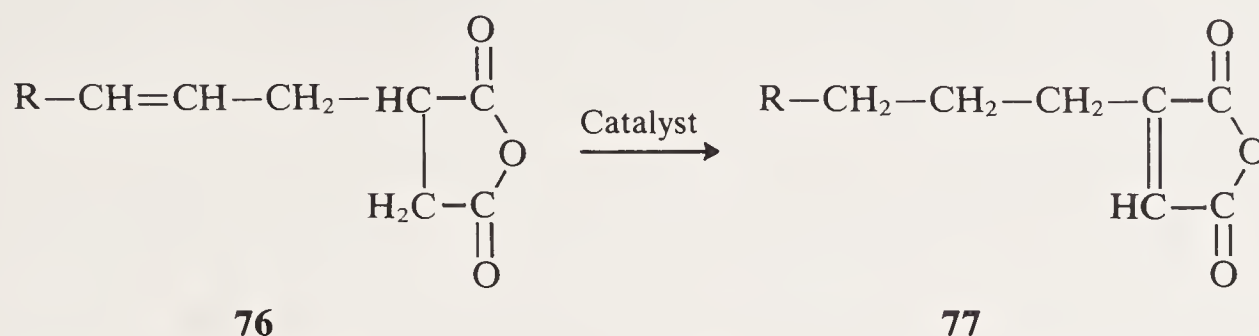


The pendant olefin function can also be utilized as a monomer in copolymerization with other olefins. Data on this are generally lacking. The diethylaluminum chloride-titanium trichloride combination has been used to make a propylene-MA **1** copolymer with good adhesion.<sup>(69)</sup> ASAs made from propylene, 1-butene, and isobutylene copolymerize with MA using radical initiation either neat or in solution.<sup>(101)</sup>

Suzuki<sup>(70)</sup> has reported that the olefin function of the alkenylsuccinic anhydride **76** can be rearranged in the presence of a palladium catalyst and a soluble base, such as trialkylamine or dialkylaniline, to give alkylmaleic anhydride **77**. Better than 40% conversion was obtained. Ruthenium catalysts



are also active for isomerization.<sup>(100)</sup> A more efficient catalyst could be advantageously employed to yield extremely interesting monomers and intermediates. Compounds such as **77** may undergo further ene reaction as well.<sup>(70)</sup>



During one such examination, Suzuki produced an alkylalkenylsuccinic anhydride by isomerization run in the presence of an olefin.<sup>(100)</sup> Since the final product did not isomerize, one wonders about the potential of a catalytic role for Ru during the ene reaction.

The anhydride function of ASAs may be easily hydrolyzed to the diacid. These and their derivatives have wetting, emulsifying, and other surfactant properties.<sup>(78)</sup> In these cases, a mixture of olefins is usually employed to obtain a reasonably priced product. Often, combination of homologues give optimum properties that are otherwise difficult to achieve from pure ASAs. Among typical olefins employed for the purpose are cracked petroleum hydrocarbons,<sup>(72-74)</sup> cracked waxes,<sup>(75)</sup> oligomers, and polymers of olefins such as propylene<sup>(76)</sup> butylenes.<sup>(62,77)</sup> In essence, most any system with an olefin function is a potential candidate. Suggested uses for products so obtained include surface-active compounds, reactive sizing for paper, engine oil lubricants, viscosity and pour-point improvers,<sup>(88)</sup> antifreeze lubricants, and moisture control for leather goods, just to name a few. A number of ASAs are now commercially available.<sup>(80,98,104)</sup> As indicated earlier, the alkali salt of the MA adduct of  $\alpha$ -methylstyrene and its dimer have been claimed to have surfactant properties.<sup>(42)</sup> Salts of ASAs have also been suggested for use in tertiary oil recovery.<sup>(81)</sup>

In addition, the alkenylsuccinic anhydrides may be converted to esters, amides, imides, etc., and each is capable of modification for a suitable application.<sup>(80)</sup> Such materials have been suggested as, for example, ashless synthetic lubricants<sup>(79)</sup> and corrosion inhibitors.<sup>(82)</sup>

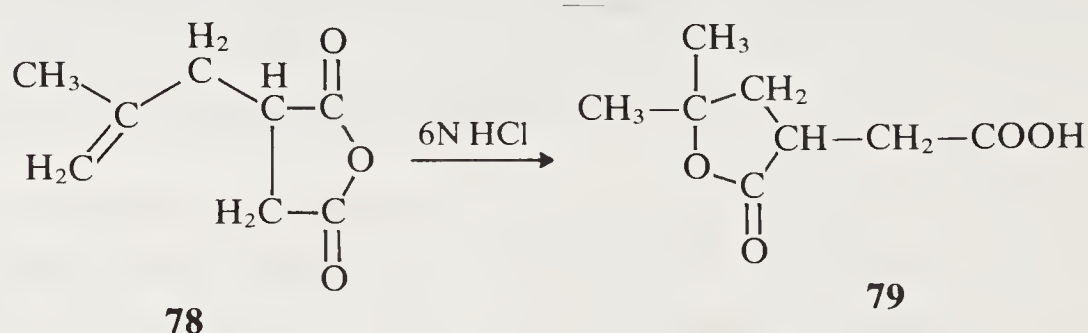
The reaction of MA with unsaturated fatty acids and glycerides and products resulting from subsequent reactions have long been utilized for applications in the varnish,<sup>(83)</sup> ink,<sup>(84)</sup> and paint<sup>(85)</sup> industries. Rapid drying characteristics needed in each of these applications may be achieved by modifying slower drying oils and alkyds with MA.<sup>(95,97)</sup> Esterification of the anhydride function is an important aspect of this chemistry. Resin acids can similarly be modified with MA or its derivatives.<sup>(94)</sup> Here, the Diels-Alder reaction plays a significant role in the modifying aspect<sup>(84)</sup>; however, the



products so obtained are used as gloss promoters, bodying, tackifying, and as hardening agents and penetration retardants for inks.

Butadiene polymers and copolymers have been treated with MA<sup>(86)</sup> (see Chapter 11). The adduct was treated with an amino alcohol and the product so obtained was suggested as a synthetic drying oil. Petroleum resin polymers have similarly been treated with MA and then with glycerine to obtain products for similar applications.<sup>(87)</sup> Copolymers or olefins with unconjugated dienes<sup>(89)</sup> have also been grafted with MA. A number of additional applications such as adhesives, resins, and polymer-modifying agents have been suggested.

In some cases, as with isobutenylsuccinic anhydride **78**, the hydrolysis with acid gives a 78% yield of the lactone **79**.<sup>(9)</sup> Products such as **79** could



find a number of applications as intermediates and monomers, since the lactone function may be called on demand following the reaction of the acid moiety.

Products made from organometallic olefins (see p. 151) are new and unique and their potential is unexplored. One can envisage incorporation of metal into polyesters this way.

## 5.9. EPILOGUE

The foregoing description of the ene reaction of MA suggests a number of potential applications of the products derived in this way. The suggested uses are by no means comprehensive and new applications are constantly being reported. Suffice it to say that this reaction avails a route to new and different unsaturated anhydrides. The latter may, by manipulation of either function at will, result in products of wide-ranging applications.

# 6

## PHOTO AND RADICAL REACTIONS OF MA

### 6.1. INTRODUCTION

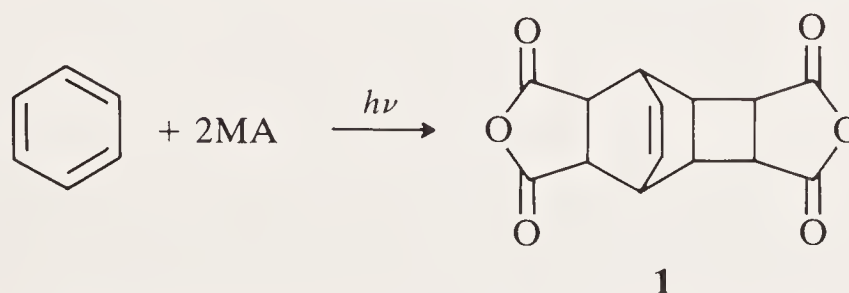
Under the influence of light, maleic anhydride can undergo reactions with a variety of substrates. Common types of reactions involve [2 + 2] cycloadditions and/or processes where radical intermediates occur. When radical intermediates do occur, often useful nonpolymeric adducts are obtained. So, in addition to the photoreactions, radical reactions of MA yielding nonpolymeric products are also discussed in this chapter.

During the photoreactions of MA, the intermediacy of an excited charge-transfer (CT) complex is frequently suggested. Due to their mechanistic relevance, a discussion of complexes of MA has been included as well.

Diels–Alder adduct formation between MA and anthracene, which is light catalyzed,<sup>(1)</sup> and that of the photodienes are discussed elsewhere.

### 6.2. PHOTOREACTIONS WITH AROMATICS [2 + 2] CYCLOADDITION

The first investigations of the photochemical reaction of MA with benzene can be credited to three groups of workers.<sup>(2–4)</sup> Thus, when a benzene solution of MA was irradiated with UV light, a 2 : 1 MA : benzene adduct was formed. The adduct has been assigned the structure **1**. Schenck and Steinmetz<sup>(3)</sup> have



shown that this reaction can be conveniently carried out using benzophenone as a sensitizer. Other sensitizers such as acetophenone, propiophenone, benzaldehyde, and diacetylbenzene have also been reported.<sup>(5–7)</sup> It has also been claimed that a mixture of benzophenone and acetone gives better yields than either alone.<sup>(8)</sup> In both the sensitized and the unsensitized processes, excitation of the CT complex was proposed.

This reaction is quite general with aromatics although earlier reports claimed that only polymeric material was produced from benzene derivatives.

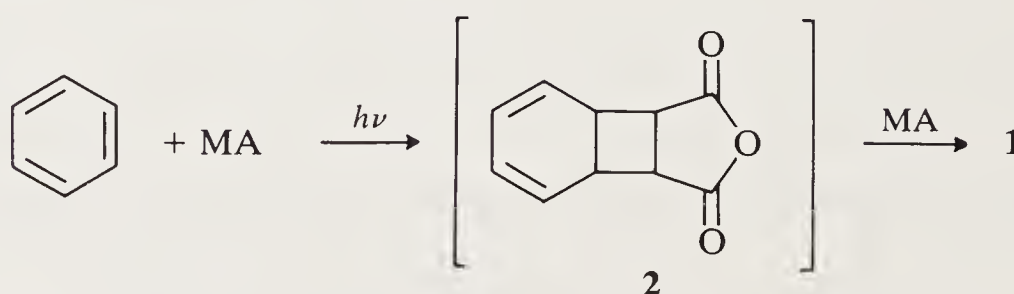
Table 6.1. Products of the Acetophenone-Photosensitized Reaction of Maleic Anhydride and Alkylbenzene in Pyrex Glass<sup>a</sup>

Alkylbenzene	Time (h)	Yield (%)	Melting point (°C)
Benzene	18	41	350
Toluene	18	29	265–270
Ethylbenzene	18	24	250–255
Cumene	18	19	245–250
<i>t</i> -Butylbenzene	18	14	—
Branched C <sub>5</sub> -C <sub>6</sub> alkylbenzene (oronite)	70	30	Gum
<i>n</i> -C <sub>10</sub> -C <sub>13</sub> alkylbenzene (oronite)	47	14	180–200

<sup>a</sup> Reprinted with permission from *J. Org. Chem.* **31**, 3974 (1966). Copyright © 1966, American Chemical Society.

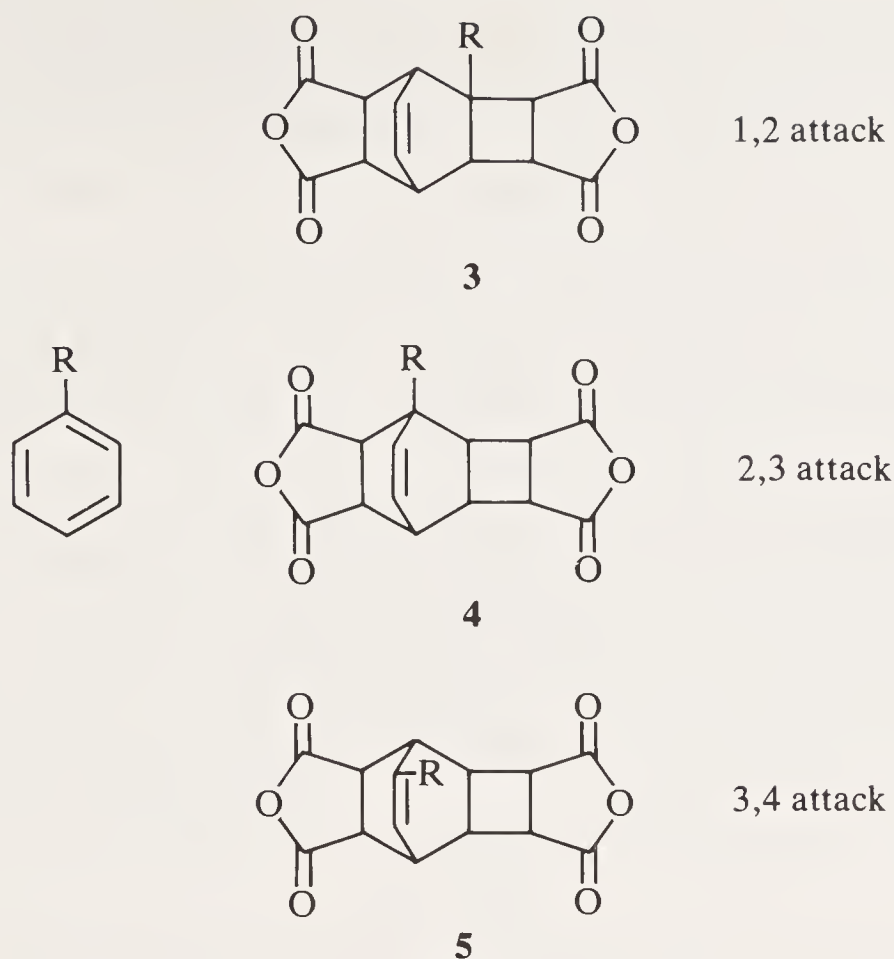
A number of substituted benzene derivatives have since been reported to undergo formation of the diadduct. Table 6.1 summarizes the adduct yields from various substituted benzene derivatives obtained by Bradshaw.<sup>(7)</sup>

It has generally been assumed that the first step in the photoreaction is the formation of a cyclobutane adduct **2**. The latter being a diene undergoes a Diels–Alder reaction to give the final adduct **1**. That the diene **2** does undergo the required DA reaction has been shown.<sup>(11)</sup> (See Sec. 6.2.2 for the mechanism.)



In the case of substituted benzenes, the position of attack is quite important. Thus, as illustrated below, initial 1,2, 2,3, or 3,4 attack will give final adducts **3**, **4**, or **5** respectively. Bryce-Smith and Gilbert,<sup>(9)</sup> based on spectroscopic evidence, have assigned structure **5** to the adduct formed with diphenyl ( $R = \text{Ph}$ ). Bradshaw<sup>(7)</sup> also studied the reaction of alkylbenzenes with MA sensitized with acetophenone. He confirmed that the adduct forms with an initial attack at positions 3,4. However, Bryce-Smith and Gilbert<sup>(12)</sup> later showed that toluene, *o*-xylene, and *p*-xylene each gave two thermally stable isomers on benzophenone-sensitized reaction with MA. Furthermore, the composition of the isomers changed with temperature as illustrated in Table 6.2. Under ambient conditions for toluene and *o*-xylene, it appears that the preferred attack is at positions 3,4 with smaller amounts of product due





to attack at unsubstituted 2,3 positions. At higher temperature, the isomer ratio changes since the ease of attack at positions 2,3 increases as shown in Table 6.2.

In the case of *p*-xylene, reaction at low temperature forms the adduct at the unsubstituted 2,3 positions. A much smaller amount of the adduct corresponding to 1,2 attack is obtained. Note that in this case one of the carbons involved in attack is substituted. At higher temperature a dramatic reversal takes place in the ease of attack as reflected in the change in isomer ratio from 20:1 to 1:10 as is shown in Table 6.2. Bryce-Smith and Gilbert<sup>(12)</sup> obtained these data on composition by isolation and fractional recrystallization. Therefore, it is not clear whether in the earlier studies the unreported isomer was not isolated or not identified; i.e., was the yield higher than they reported earlier?

Table 6.2. Temperature Dependence of Position of Attack in Alkylbenzenes<sup>a</sup>

Compound	Isomer ratio		Remark
	20°C	100°C	
Toluene 3,4/2,3	1:1	3:2	Sensitized
	4:1		Unsensitized
<i>o</i> -Xylene 3,4/2,3 <sup>b</sup>	1:1	2:1	Sensitized
<i>p</i> -Xylene 2,3/1,2	20:1	1:10	Sensitized

<sup>a</sup> From Reference 12.

<sup>b</sup> By IUPAC system 2,3 and 3,4 in *o*-xylene will correspond to 3,4 and 4,5, respectively.

Sifinades *et al.*<sup>(13,14)</sup> have also observed the photoadduct in the product mixture obtained from the reaction of MA with benzene or alkylbenzene under a silent electrical discharge. Small amounts of photoadducts have also been reported to form on exposure of a benzene solution of MA to  $\gamma$  irradiation.<sup>(15,130,131)</sup>

Photoreactions of a number of benzene derivatives have been examined.<sup>(9)</sup> Relative rates of the adduct formation in the sensitized and unsensitized processes for some aromatic compounds are given in Table 6.3. One obvious feature of Table 6.3 is that all substituents on the benzene nucleus decrease the rate of both the sensitized and unsensitized reaction. Furthermore, benzene with electron-withdrawing substituents (CN, NO<sub>2</sub>, COOR, COR) did not form either the adduct or the charge-transfer complex. Chlorobenzene, however, which did form an adduct, also formed a charge-transfer complex. Russian workers<sup>(10)</sup> have shown that both chlorobenzene and fluorobenzene partake in the reaction to form the 1:2 MA adduct. Phenol was reported not to form an adduct but small quantities of product might have gone unnoticed.<sup>(9)</sup>

Table 6.3. Relative Rates of 2:1 Photoaddition of Maleic Anhydride to Some Aromatic Compounds at 30°C, Unsensitized, and Sensitized by Benzophenone<sup>a</sup>

Aromatic compounds	Unsensitized	Sensitized	$\lambda_{\max}$ (m $\mu$ ) CT complex
Benzene	0.38	(1.0)	278
Toluene	0.12	0.5	284
<i>t</i> -Butylbenzene	0	0.25	290
Chlorobenzene	0	0.25	305
Biphenyl <sup>b</sup>	0.05	0.12	295
Phenol <sup>c</sup>	0	0	330
Benzonitrile	0	0	No complex
Nitrobenzene	0	0	No complex
Methyl benzoate	0	0	No complex
Acetophenone	0	0	No complex
<i>o</i> -Xylene	0	0.15	288
<i>p</i> -Xylene	0	0.08	290
Quinol <sup>d</sup>	0.02	0.07	335
Durene <sup>e</sup>	0	0	360
Hexamethylbenzene <sup>e</sup>	0	0	408
Biphenylene <sup>e</sup>	0	0	No complex
Naphthalene <sup>e</sup>	0	0	298

<sup>a</sup> From Reference 9.

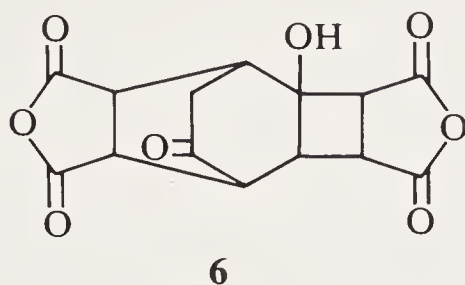
<sup>b</sup> In cyclohexane.

<sup>c</sup> At 50°C.

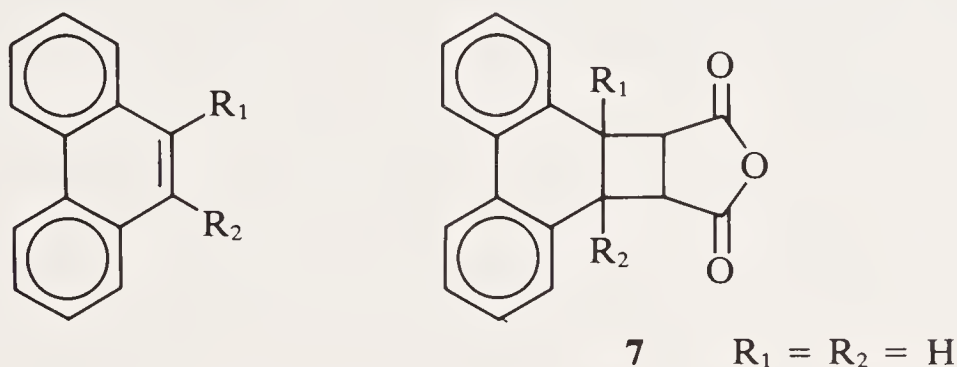
<sup>d</sup> At 70°C.

<sup>e</sup> In cyclohexane at 30°C and in melts at 80°C.

Hydroquinone (HQ) has also been reported to form a 1 : 2 MA adduct.<sup>(9)</sup> The structure of this was proposed to be **6** based on spectral data. Thus, the initial attack must occur preferentially at the 1,2 positions.



A number of other aromatic compounds have been reacted with MA under the influence of light. Bryce-Smith and Vickery<sup>(16)</sup> have shown that phenanthrene does add MA under the influence of UV light in the presence of a sensitizer to give the adduct **7**. No yield was mentioned. They indicated that benzil (which does not sensitize the benzene-MA reaction) was a better sensitizer than benzophenone.



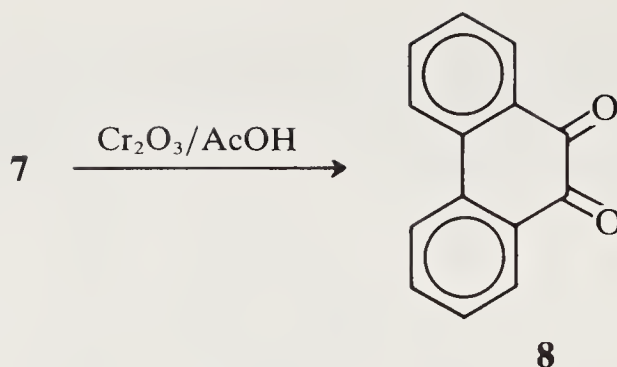
Melikadze *et al.*<sup>(17)</sup> have studied a series of 9- and 10-substituted phenanthrenes. The yield data of their work are given in the Table 6.4. The addition to 9,10 positions of phenanthrene was proved by oxidation of the adduct to phenanthraquinone **8** and by spectroscopy.<sup>(16,17)</sup> The addition with phenanthrene is general so that the dialkyl esters of maleic and fumaric acids can be

Table 6.4. Photoreactions of Mono and Dialkylphenanthrenes with MA to **7**<sup>a</sup>

$R_1$	$R_2$	Yield (%)
$C_2H_5$	H	40.0
$C_3H_7$	H	39.5
$C_5H_{11}$	H	39.0
$C_2H_5$	$C_2H_5$	62.0
$C_4H_9$	$C_4H_9$	60.0

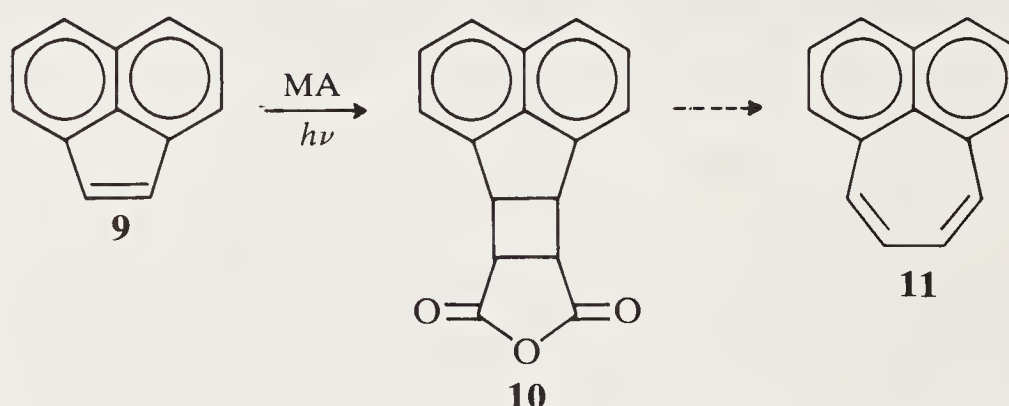
<sup>a</sup> From Reference 17.





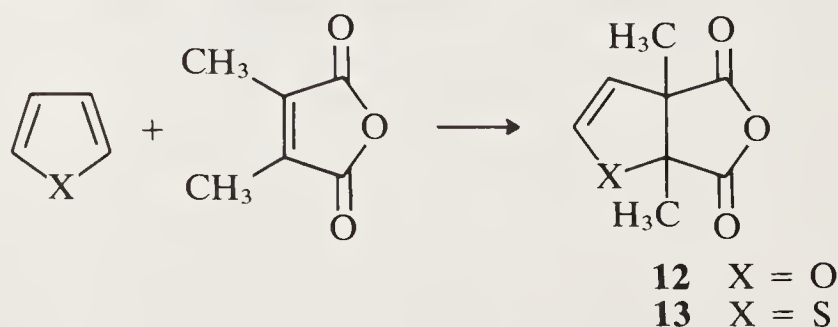
utilized as well.<sup>(18)</sup> Adducts like **7** revert to starting hydrocarbon when heated to 500°C.<sup>(17)</sup> Fumarate ester reportedly yields an oxetane product.<sup>(29)</sup> Unwarranted conclusions about the seasonal nature of the reaction of MA with alkyphenanthrene have been reported<sup>(143)</sup>; it may be that the product was partially hydrolyzed.

In an interesting approach to pleiadiene **11**, Shields *et al.*<sup>(19)</sup> have utilized photochemical addition of MA to acenaphthene **9** to give **10**.



Indene reacts with MA at  $-70^\circ\text{C}$  in the presence of a benzophenone sensitizer in acetone to give 86% yield of the corresponding adduct.<sup>(139)</sup>

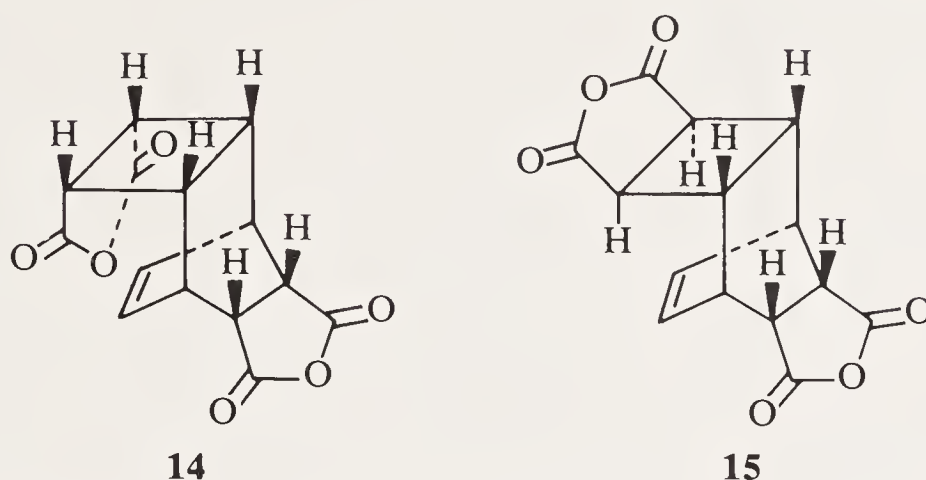
It may be of interest to note that dimethylmaleic anhydride reacts with furan<sup>(20)</sup> and thiophene<sup>(21)</sup> under the influence of light to yield the [2 + 2] addition products: cyclobutane derivatives **12** and **13**, respectively. Although the analogy of MA with dimethylmaleic anhydride was indicated, no adducts with MA were mentioned in these reports.



### 6.2.1. Stereochemistry of the Photoadduct

It was indicated earlier that a diene intermediate is proposed to form on photochemical cycloaddition of MA to benzene. The diene subsequently reacts with another mole of MA to form the observed diadduct. Thus, even if the

DA reaction was to give exclusively an *endo* product, two possible products, **14** and **15**, could form. On the basis of extensive spectroscopic and chemical



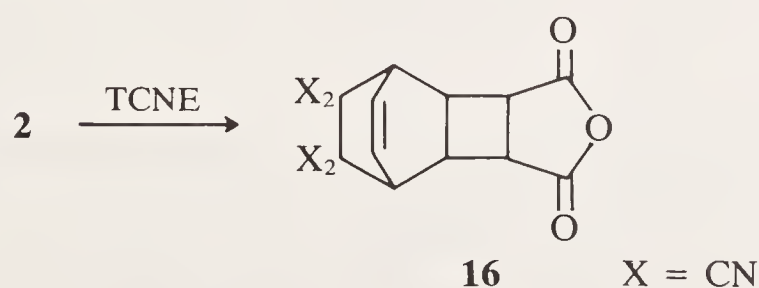
evidence, Grovenstein *et al.*<sup>(4)</sup> proposed that the photoaddition is *exo* stereospecific so structure **15** is the correct formulation of the photoadduct. Bryce-Smith and coworkers<sup>(22,23)</sup> later confirmed this structure through a detailed study of the system. A similar steric conclusion has been advanced by Bryce-Smith and Gilbert<sup>(9)</sup> for the alkylbenzene:MA photoadducts.

In the reaction of phenanthrene derivatives,<sup>(16,17)</sup> although *syn* and *anti* geometries are possible, originally no stereochemistry of the adduct was specified. Recently, Creed *et al.*<sup>(29)</sup> have confirmed the phenanthrene:MA adduct to be *cis-exo*, hence, *anti* geometry was preferred. Shields *et al.*<sup>(19)</sup> showed that with acenaphthene, adduct formation, which is solvent dependent, gave more *anti* product.

### 6.2.2. Mechanism

It was recognized quite early that the mechanism of the sensitized and unsensitized photoreactions are different. Bryce-Smith and Lodge<sup>(22)</sup> showed that unsensitized reaction is not affected by the presence of O<sub>2</sub> while, on the other hand, the sensitized reaction is inhibited by O<sub>2</sub>. Thus, the unsensitized reaction was believed to be singlet in character whereas the sensitized process was considered to proceed through a triplet.

The presence or absence of the diene intermediate has caused some confusion in the past. Hardham and Hammond<sup>(6)</sup> failed to trap the diene **2**



with methyl acrylate or tetracyanoethylene (TCNE). Bryce-Smith<sup>(24)</sup> also mentioned failure to trap the diene with TCNE to obtain the mixed adduct

Table 6.5. Photoreaction of MA with Benzene in the Presence of TCNE<sup>a</sup>

MA (m)	TCNE (m)	Solvent	<b>1</b> (mol %)	<b>16</b> (mol %)
0.5	0.1	Benzene	88	12
0.375	0.1	Benzene	85	15
0.25	0.1	Benzene	79	21
0.1	0.1	Benzene	59	41
0.02	0.1	Benzene	23	77
0.5	0.1	CH <sub>2</sub> Cl <sub>2</sub>	50	50

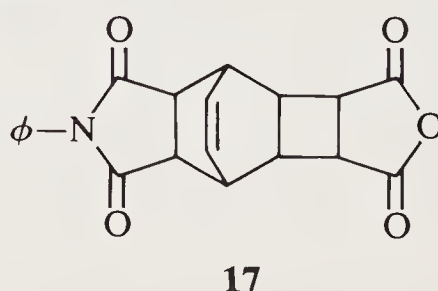
<sup>a</sup> From Reference 25.

such as **16**. The dienophile TCNE was proposed to be particularly useful since:

- It does not form a photoadduct with benzene or MA.
- 1,3-cyclohexadiene reacts more readily with TCNE than MA.

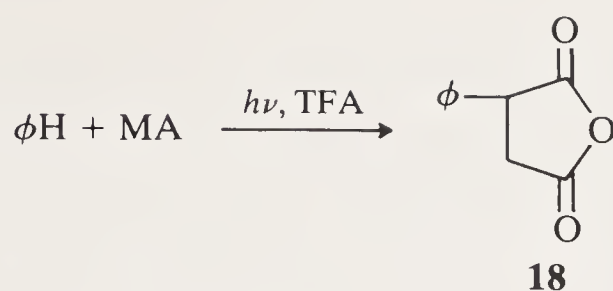
Hartmann *et al.*<sup>(25)</sup> have shown that the diene **2** can react with TCNE. However, the yields are modest unless the system is diluted with dichloromethane as shown in Table 6.5. Thus, earlier failure to trap the diene resulted from an unusually low dienophilic activity of TCNE in benzene attributed to the charge-transfer complex formed between the two.

Bryce-Smith and coworkers<sup>(24,26)</sup> have also shown that the relative quantum yields of the benzene:MA adduct formation is much more enhanced in dibromomethane. They have further shown that the initial  $\phi$ H:MA photoadduct can be better trapped by *N*-phenylmaleimide. Thus, irradiation of a benzene solution of 0.17 *M* in MA and 0.0846 *M* in *N*-phenylmaleimide in the presence and absence of dibromomethane gave 1:1:1 adduct **17** as the only detectable product.



Interestingly, the unsensitized process in dibromomethane–benzene solvent can not only be severely inhibited by the presence of trifluoroacetic acid (TFA), but the course of the reaction can be completely altered such that phenylsuccinic anhydride **18** rather than the diadduct **1** is formed.<sup>(27)</sup> The sensitized reaction, on the other hand, is affected much less by the presence of TFA.





Hardham and Hammond<sup>(5,6,28)</sup> have examined a variety of sensitizers and inhibitors. It was shown that sensitizers having excitation energy greater than 66 kcal/mole sensitize the reaction while those with less energy do not sensitize. This is demonstrated in the Table 6.6. The failure of triphenylene to sensitize has been ascribed to probable errors in measurement of triplet excitation energies. Furthermore, since 72 kcal/mole would be required to excite  $\text{MA} \rightarrow \text{MA}^\tau$ , the sensitization of the reaction with benzophenone suggests excitation of the charge-transfer complex. In addition, it was observed by Bryce-Smith *et al.*<sup>(136)</sup> that the yield of the adduct **1** decreases on dilution with cyclohexane which decreases the concentration of the complex.

Table 6.6. Yields of Addition Product **1** Obtained by Irradiation of Solutions of Maleic Anhydride in Benzene in the Presence of Various Additives<sup>a</sup>

Additive	Concentration of additive (M)	Yield of product (mg)	Triplet energy
<b>Sensitizers</b>			
propiophenone	0.80	26	74.7
xanthone	0.01	14	74.2
acetophenone	0.80	41	73.6
benzaldehyde	0.30	36	71.9
benzophenone	0.050	46	68.5
4,4'-dichlorobenzophenone	0.050	59	68.0
<i>p</i> -diacetylbenzene	0.30	35	67.7
<i>p</i> -cyanobenzophenone	0.050	40	66.4
<b>Inhibitors</b>			
triphenylene	0.10	0	66.6
thioxanthone	0.05	0	65.5
anthraquinone	0.10	0	62.4
2-acetylfluorene	0.10	0	62.6
naphthalene	0.10	0	60.9
2-acetonaphthone	0.20	0	59.3
chrysene	0.01	0	56.6
benzil	0.050	0	53.7
fluorenone	0.10	0	53.0

<sup>a</sup> Reprinted with permission from *J. Am. Chem. Soc.* **89**, 3200 (1967). Copyright © 1967, American Chemical Society.

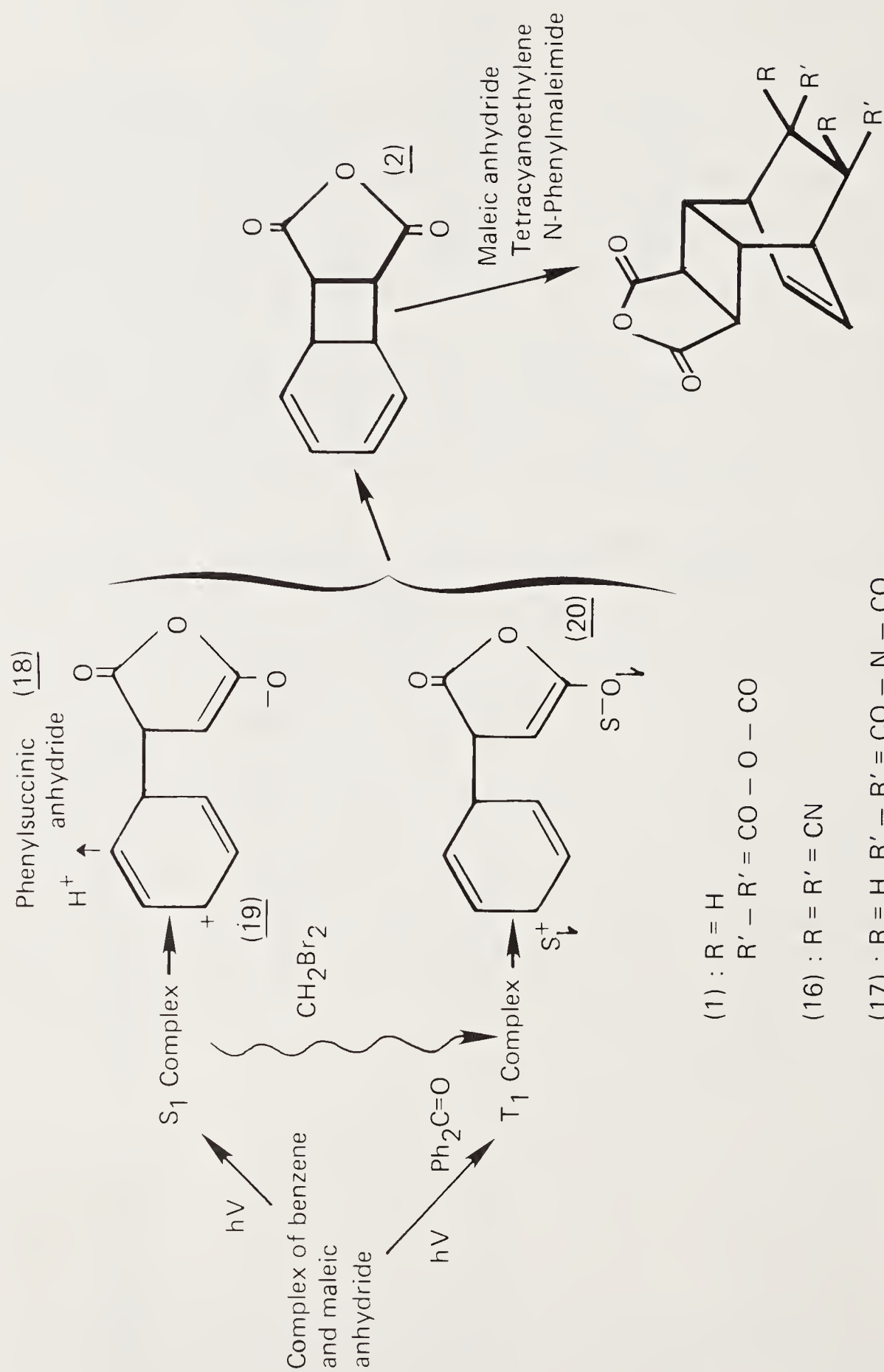
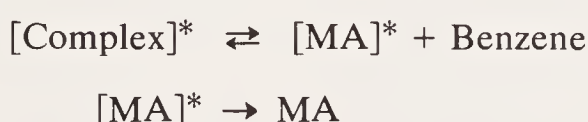


Fig. 6-1. Products of photoreaction of MA with benzene. From Reference 26.

The above observations can be rationalized as follows<sup>(27)</sup>: The irradiation of a benzene:MA charge-transfer complex gives an excited-singlet complex in the case of unsensitized reaction. The sensitized reaction, on the other hand, goes through an excited-triplet complex. The latter is produced by the energy transfer from the excited triplet of the sensitizer as shown in the scheme in Fig. 6-1. The singlet state being relatively more polar can go through a dipolar intermediate **19** which when trapped with a proton would yield the observed phenylsuccinic anhydride **18**.

The triplet state is relatively less polar since spin considerations require that a triplet should be formulated as a diradical rather than a zwitterion **19**.<sup>27</sup> Thus, the intermediate **20** would be little affected by acid. Hence, it may be concluded that the unsensitized  $\phi\text{H}:\text{MA}$  reactions go through a zwitterionic intermediate **19**. The latter may make some contribution during the sensitized reaction. The role of dibromomethane in the unsensitized reaction, therefore, is to aid the intersystem crossing.

The quantum yield of benzene:2MA reactions are low ( $<0.1$ ). Since the quantum yields show a slight dependence on MA concentration, it may be inferred that the reversal of monoadduct formation competes with the diadduct formation.<sup>(5)</sup> However, this is not likely to account for the inefficient reaction. Based on a detailed study of the effect of sensitizers, their concentration, dilution with cosolvents, etc., Hardham and Hammond<sup>(6)</sup> suggest that the inefficiency of the process results after the energy has been transferred to the complex. One possibility is the loss of excitation as follows:



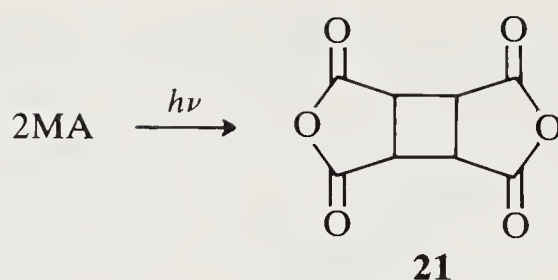
The breakdown of the complex into constituents would be endothermic based on their data. Therefore, a small decrease in the quantum yield on increasing reaction temperature may be due to this factor. This explanation is far from complete and more work is warranted to understand the reasons for and cures of this inefficiency.

## 6.3. PHOTOREACTIONS WITH OLEFINS AND ACETYLENES

### 6.3.1. Reactions with Olefins

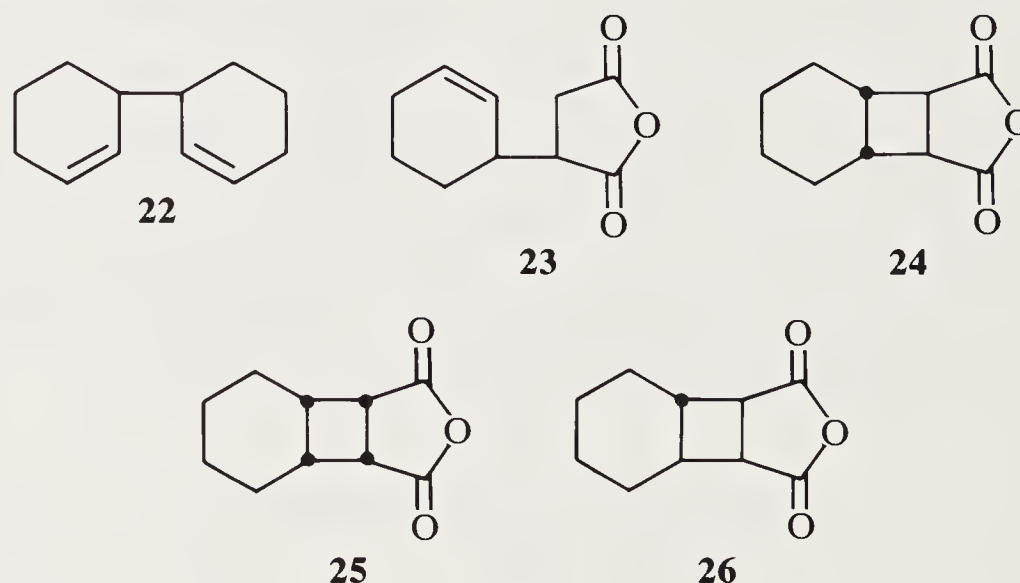
The first investigation of the photoreaction of maleic anhydride with an olefin can be credited to Griffin and coworkers.<sup>(30)</sup> It was observed that a thin layer of MA deposited on glass, upon exposure to an UV lamp, produced a dimer **21**.





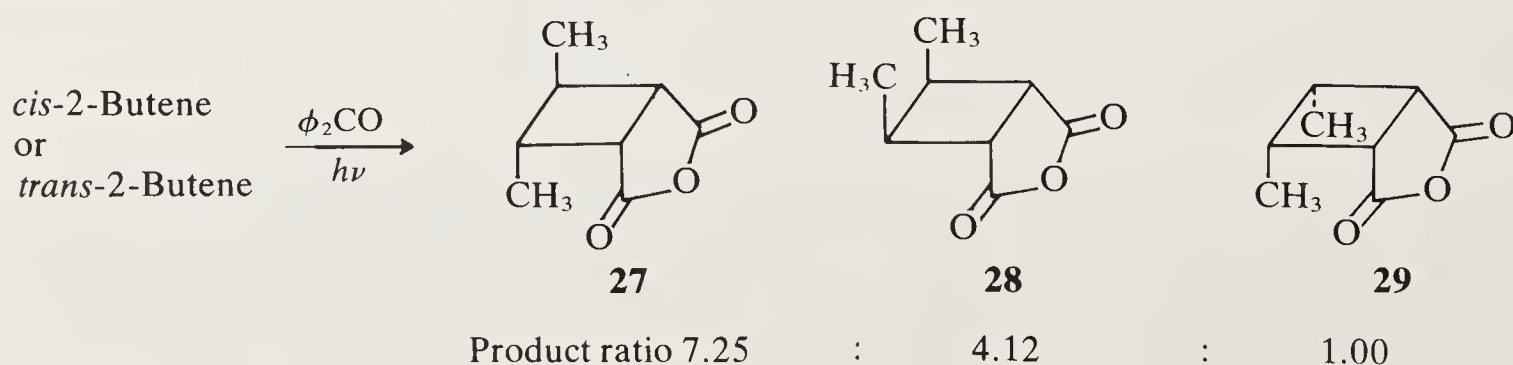
It has since been found that dimer **21** is a by-product of a number of photoreactions of MA. The dimerization has recently been studied in detail by Boule and Lemaire.<sup>(80)</sup> They observed that in product **21**, the anhydride residues are *trans* to each other. A quantitative yield of **21** was reported in  $\text{CCl}_4$  solvent. Quantum yields of 0.5–0.6 (333  $\text{m}\mu$ ) for the disappearance of MA were independent of MA concentration above  $2 \times 10^{-3} \text{ M}$ . Dimerization is reported to be an exclusive process in  $\text{CHCl}_3$  and  $\text{CCl}_4$ .<sup>(121)</sup>

Robson and coworkers<sup>(31)</sup> observed that upon irradiating a solution of MA in cyclohexene, the following products were obtained:



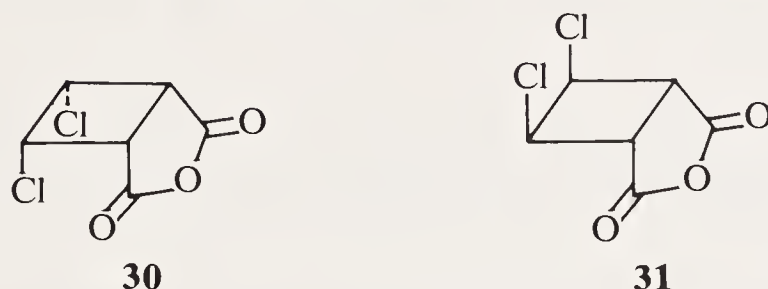
Robson *et al.*<sup>(31)</sup> showed that the products were formed from the excited charge-transfer complex because the irradiation of the samples was done at  $\lambda > 285 \text{ m}\mu$ . In this range, 98% of all incident light is absorbed by the charge-transfer complex and no significant absorption by individual components is observed.<sup>(31)</sup>

Pless<sup>(32)</sup> showed that a cyclic derivative can also be formed from *cis*- and *trans*-2-butene. Either, when subjected to a benzophenone-sensitized reaction with MA, gave the same ratio of the following products. Modest yields of the products were obtained.



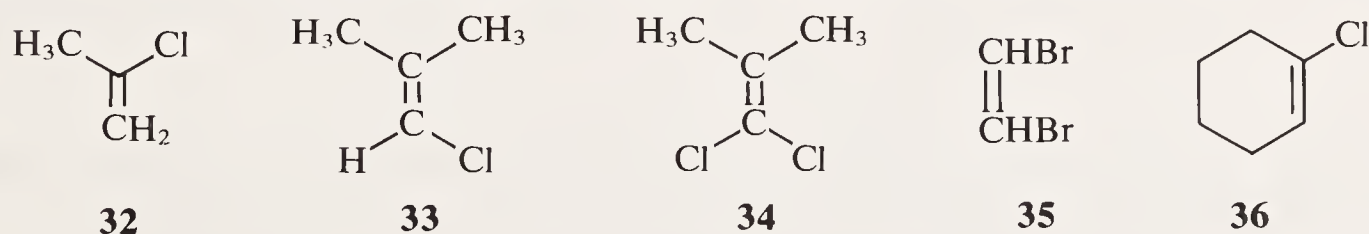
Similar reaction was also reported with *cis*- and *trans*-3-hexene. The loss of geometry of the starting olefin was proved not to be due to prior isomerization of the olefin. Thus, starting with *trans*-olefins, no *cis*-olefin was detected in the reaction mixture. When *cis*-olefin was the starting material only a small amount (ca. 7%) was observed to isomerize.

Steinmetz and coworkers<sup>(33)</sup> have shown that *cis*-1,2-dichloroethylene undergoes photoreaction with MA when sensitized with benzophenone. Two stereoisomeric *cis*-dichlorocyclobutanes, namely, *syn* **30** and *anti* **31** isomers, were isolated as products in 81:19 ratio. Obviously, the geometry of the

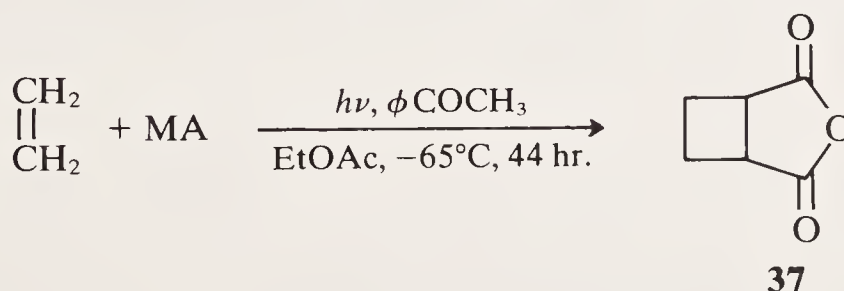


starting olefin was retained in the product. The distribution of *syn/anti* was dependent on the solvent: for example, in acetonitrile, **30** was the only product while in carbon tetrachloride, **31** was obtained as the chief product. The retention of the olefin geometry is in direct contrast to Pless' observation for nonhalogenated olefins.<sup>(32)</sup> Interestingly, *trans*-1,2-dichloroethylene gave the same products which were obtained from the *cis* derivative suggesting a preisomerization of the olefin,<sup>(33)</sup> again in contrast to Pless'<sup>(32)</sup> observation.

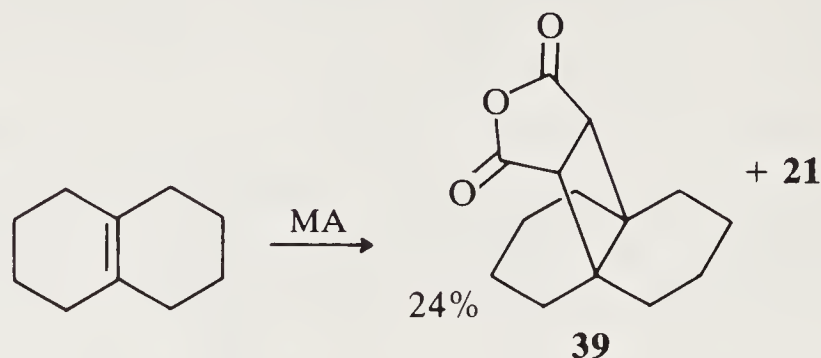
A number of other halogenated olefins were examined by Steinmetz *et al.*<sup>(33)</sup> Each of the 1-haloolefins gave the desired cyclobutane derivative. The olefins used included 2-chloropropylene **32**, 1-chloroisobutylene **33**, 1,1-dichloroisobutylene **34**, *cis*- and *trans*-1,2-dibromoethylene **35**, and 1-chlorocyclohexene **36**. A halogen atom in the molecule helps prevent copolymerization during the photoreaction.<sup>(33)</sup> Furthermore, Steinmetz also stated that no reaction occurred in the absence of benzophenone sensitizer.



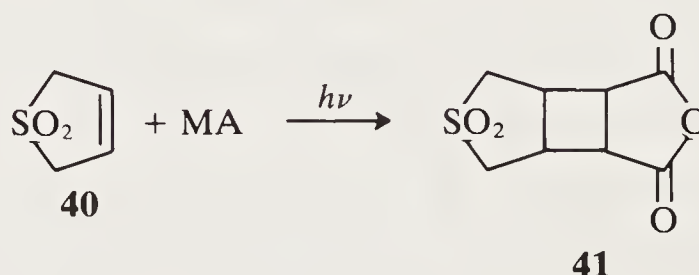
Ethylene has been reported to add MA in ethyl acetate at  $-65^{\circ}\text{C}$ . Owsley and Bloomfield<sup>(34,77)</sup> reported a 71% yield of the cyclobutane derivative **37**. In ether as a solvent, no adduct was obtained, only a white polymer was formed.



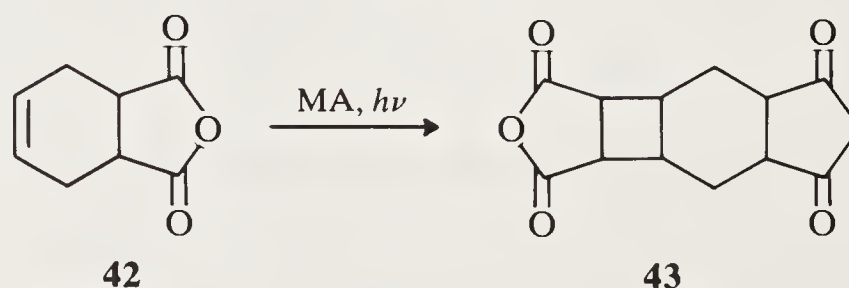
Photocycloaddition of MA to 9,10-octalin **38** has been recently reported by Kunai and coworkers.<sup>(44)</sup> MA dimer **21** is also observed.



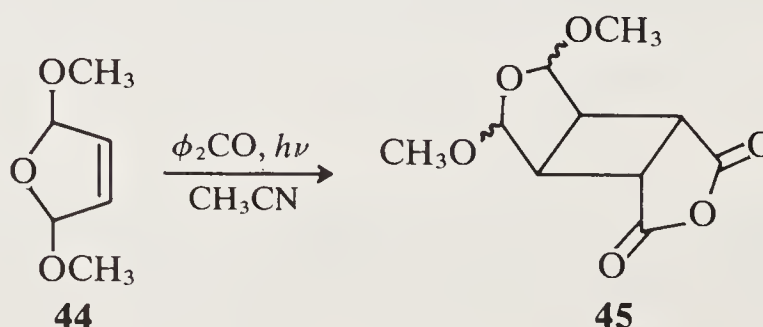
Shaikhrazieva *et al.*<sup>(35)</sup> have reported cyclobutane adduct **41** formation from 2,5-dihydrothiophene-1,1-dioxide **40** and MA under the influence of



light. These Russian workers<sup>(36)</sup> also reported that a photoreaction of 1,2,3,6-tetrahydrophthalic anhydride **42** with MA yields a tetracarboxylic acid dianhydride **43**. It may be recalled that **42** is obtained in quantitative yield by a Diels–Alder reaction of butadiene with MA.



Hinshaw<sup>(37)</sup> obtained a 40% yield of the adduct **45** on sensitized irradiation of MA and 2,5-dimethoxy-2,5-dihydrofuran **44** in acetonitrile.

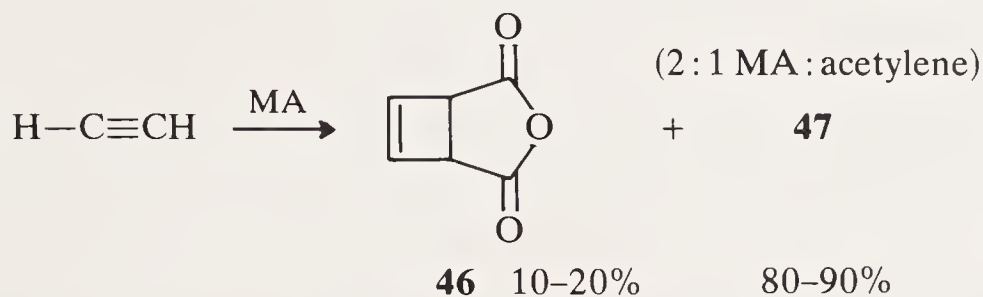


Interesting spiro compounds are formed on cycloaddition of MA to methylene cyclopropane<sup>(81)</sup> and diketene.<sup>(138)</sup>

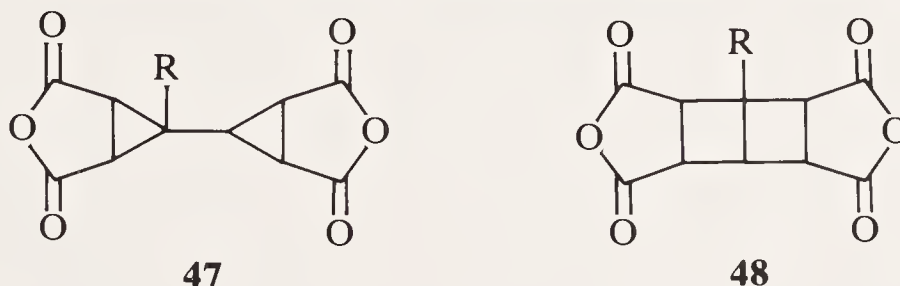


## 6.3.2. Reactions with Acetylenes

Koltzenburg *et al.*<sup>(38)</sup> have shown that sensitized photoaddition of MA to acetylene gives, in addition to the cyclobutene derivatives **46**, a 2:1 MA:acetylene derivative **47**. They further showed that the cyclobutene adduct

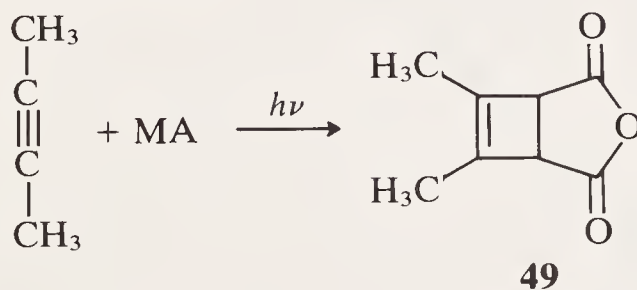


could react with MA under the influence of UV radiation to form an adduct **48** which is proposed to be a bicyclohexane derivative based on cycloaddition of MA with olefins. Therefore, the adduct **47**, which is isomeric with **48**, was given the following structure based on spectroscopic evidence.

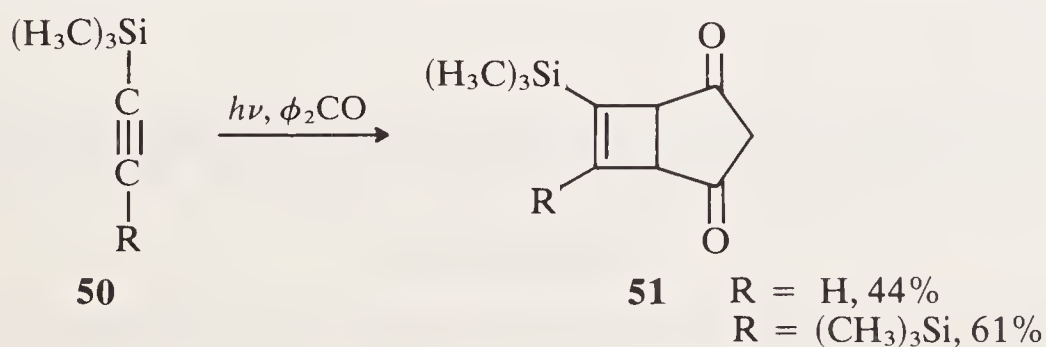


Hartmann<sup>(42,43)</sup> showed that only acetylene (R = H) and methylacetylene (R = methyl) form adducts such as **47**. Higher-terminal acetylenes give exclusive formation of cyclobutene adducts. Bloomfield *et al.*<sup>(78)</sup> obtained a 70% yield of the cyclobutene adduct **46** (R = H) by the reaction of acetylene with MA in acetophenone-ethyl acetate solution.

Pless<sup>(32)</sup> and Criege *et al.*<sup>(40)</sup> have also investigated the photoreactions of acetylenes with MA. Butyne-2 was reported by the latter group to give 95% of the cyclobutene derivatives **49**.



Photoaddition of MA to acetylenes has been also extended to trimethylsilylacetylenes **50** by Birkofer and Eichstaedt<sup>(45)</sup> to obtain **51**.



It may be of interest to note that the reaction of MA is typical of several unsaturated anhydrides<sup>(34)</sup> and derivatives both with olefins and acetylenes. For example, maleimides<sup>(38)</sup> and dichloromaleic anhydride<sup>(41)</sup> have also been reported to give cyclobutane derivatives.

### 6.3.3. Mechanism

The understanding of the mechanism of the photoreaction of MA with olefins and acetylene is due mainly to the work of two groups.<sup>(32,33,42,43)</sup> Pless<sup>(32)</sup> did an extensive study of the kinetics and stereochemistry of the reaction of MA with olefins. As was mentioned earlier, the same mixture of

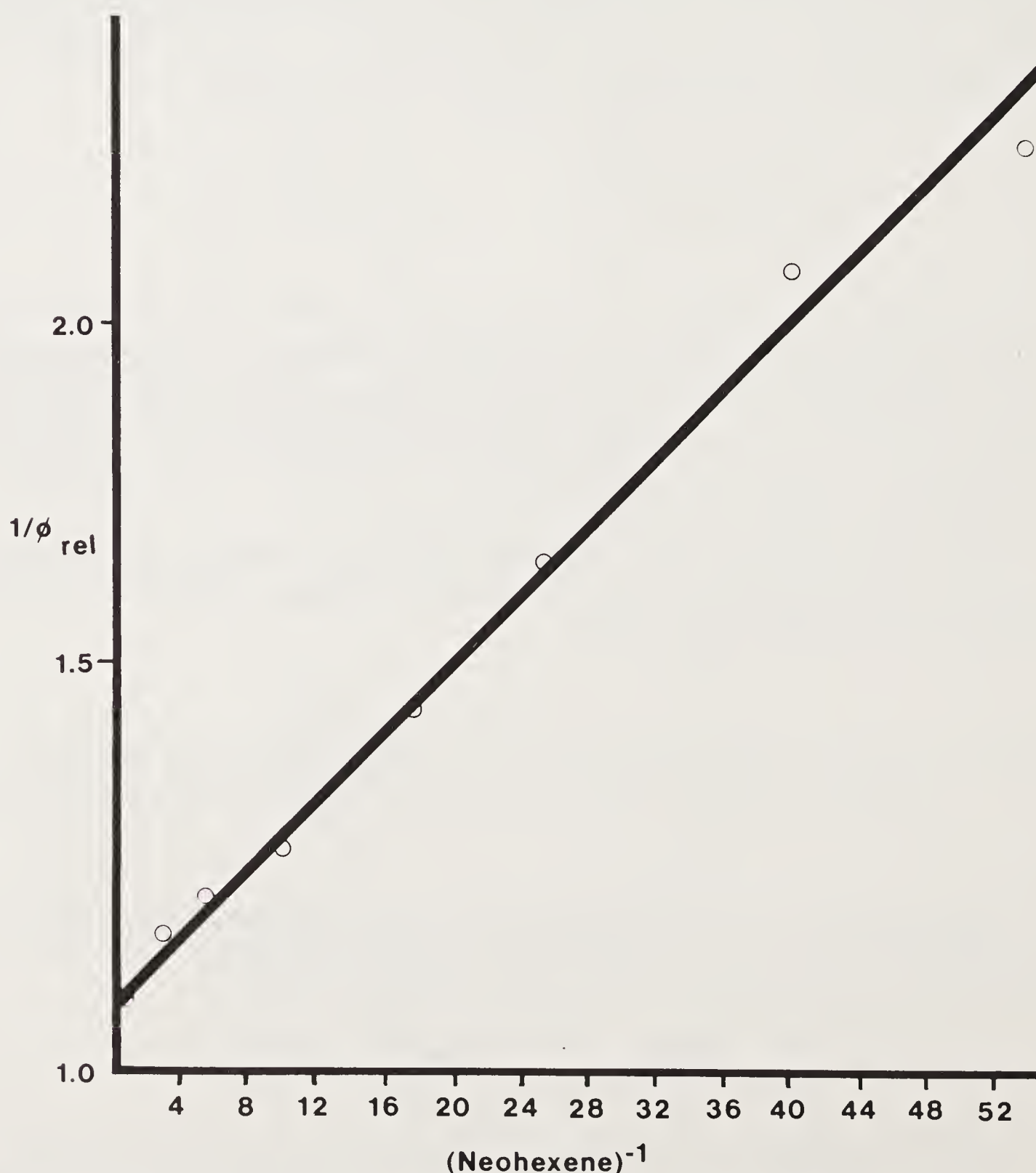
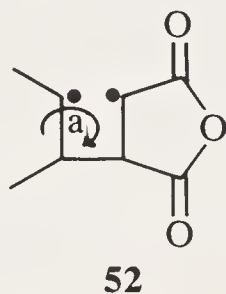


Fig. 6-2. Dependence of  $1/\phi_{\text{rel}}$  on reciprocal of neohexene concentrations. From Reference 32.

isomers was obtained starting with *cis*- or *trans*-2-butene. There was no significant isomerization of the starting olefin; it was postulated that a diradical **52** was formed which could freely rotate around the bond a. This would give rise to an equilibrium distribution of products, as was observed.



Pless<sup>(32)</sup> also observed a linear relationship between the reciprocals of concentration versus quantum yield of the reaction of MA with neohexene (Fig. 6-2), as well as 2-butyne (Fig. 6-3). A linear Stern–Volmer plot<sup>(32,135)</sup>

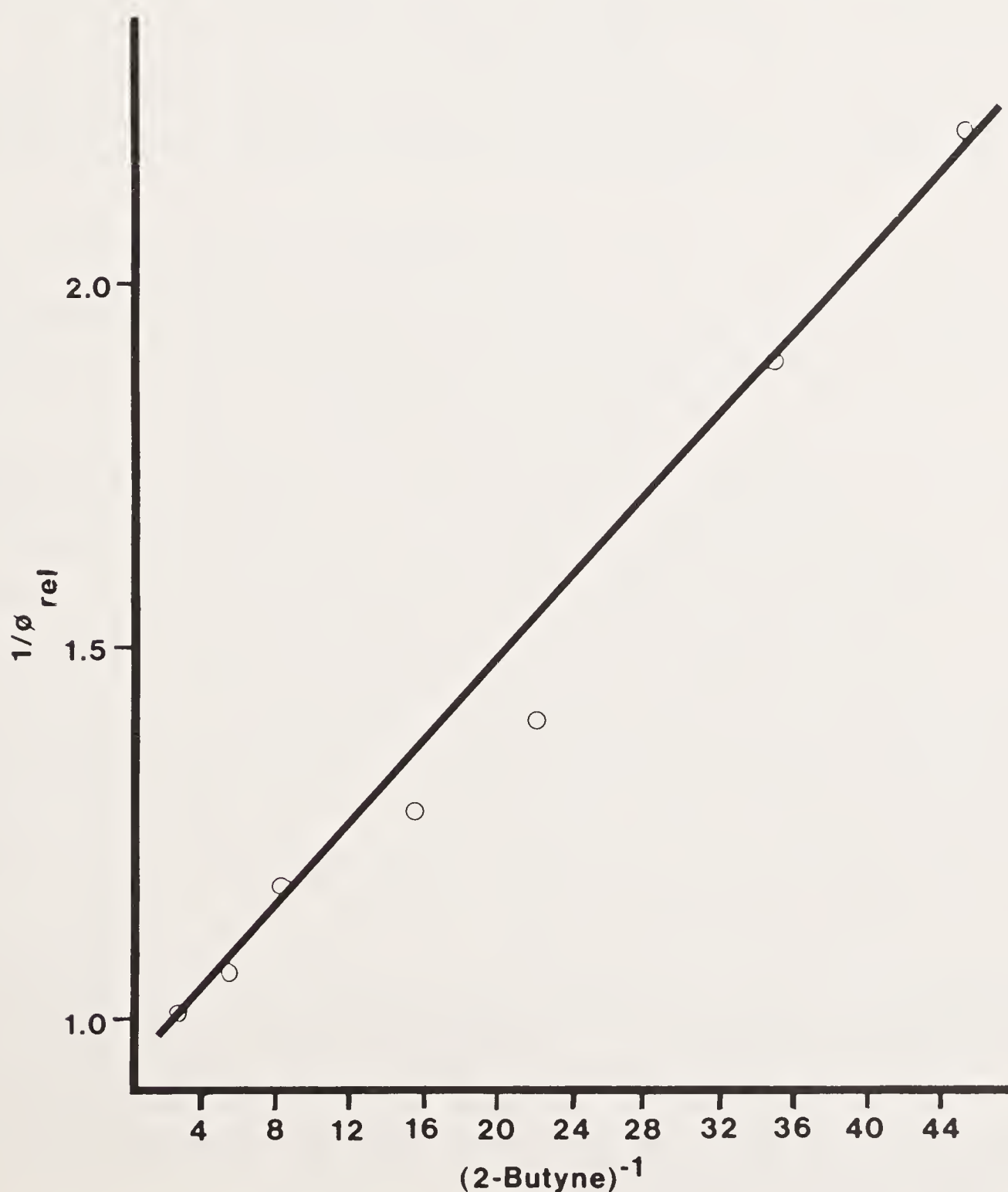
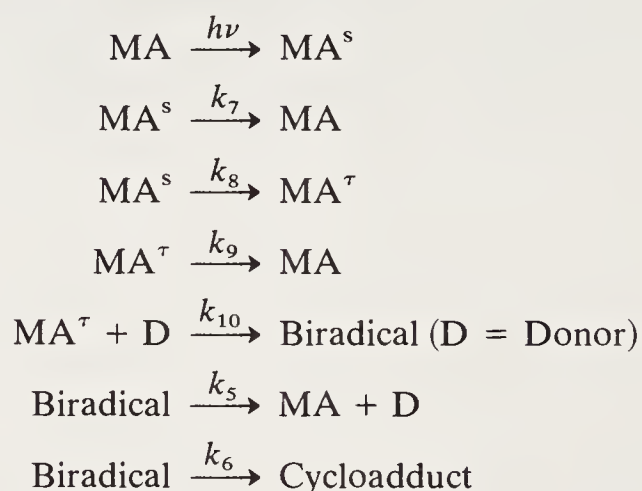


Fig. 6-3. Dependence of  $1/\phi_{\text{rel}}$  on reciprocal of 2-butyne concentration. From Reference 32.



(with 2,3-butandione employed as a quencher) for 2-butyne assured that an insignificant amount of product formation resulted from singlet MA. The latter then should produce triplet MA with high efficiency.<sup>(6)</sup> A detailed kinetic study of neohexene-MA and 2-butyne-MA reaction gave a nonlinear relationship of relative quantum yield versus donor concentration. Since this would be expected for solutions of low optical density (low concentration of charge-transfer complex), product formation resulting from the excitation of the charge-transfer complex was ruled out.

Based on these evidences, Pless<sup>(32)</sup> argued that only one scheme involving triplet MA as the primary reacting species can explain all the observations. The following general scheme was proposed:



The resulting expression given below was shown to satisfy the observations.

$$\phi = \frac{k_6}{k_5 + k_6} \frac{k_{10}[\text{D}]}{k_9 + k_{10}[\text{D}]}$$

Hartmann<sup>(43)</sup> has observed that the ratio of cyclobutene:di-cyclopropyl adducts (e.g., **46**:**47**) obtained upon irradiation of MA and acetylene or methylacetylene showed a linear relationship with inverse of MA concentration (Fig. 6-4). The passage of the plot through the origin can be reconciled only if the addition of triplet MA to acetylene occurs and is *trans*-stereospecific.

The mechanism for the product formation for ethylene and acetylene, therefore, can be represented by the schemes in Fig. 6-5.

Although the agreement is good between Pless<sup>(32)</sup> and Hartmann,<sup>(42,43)</sup> it should be remembered that no generalization of the mechanism is possible. For example, Robson *et al.*<sup>(31)</sup> have shown that the photoreaction of MA and cyclohexene involves the excitation of the charge-transfer complex. It is not clear if involvement of  $\text{MA}^\tau$  with simple olefins rather than an excited charge-transfer complex is due to lower equilibrium constant for CT complex formation. In addition, data on adducts from *cis*- and *trans*-dichloroethylenes<sup>(33)</sup> and the resulting stereochemistry are different from that observed by Pless.<sup>(32)</sup> Thus, it may suffice to say that available data are insufficient to derive a general picture at present, but with linear aliphatic nonhalogenated olefins,  $\text{MA}^\tau$  may be the key intermediate.

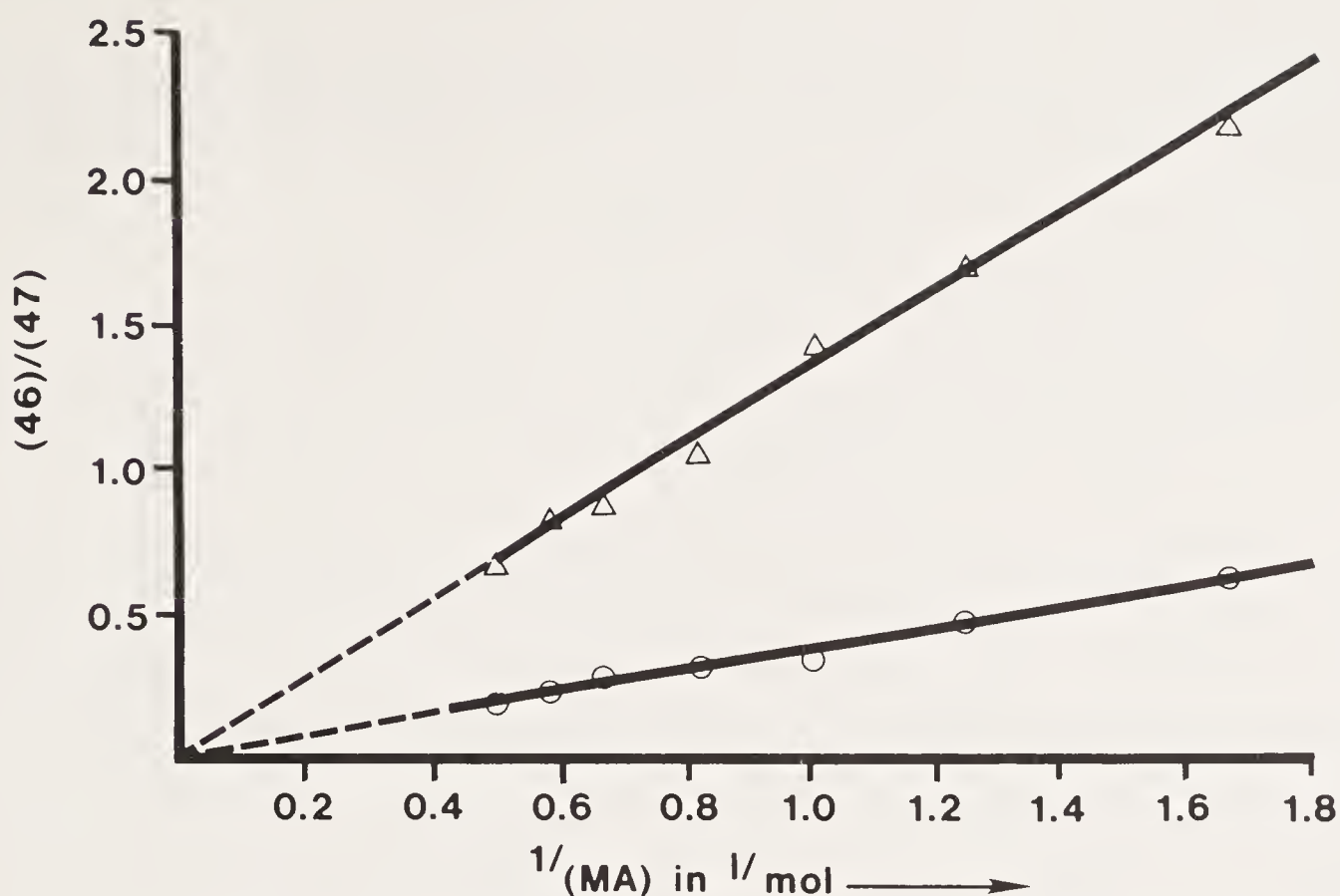
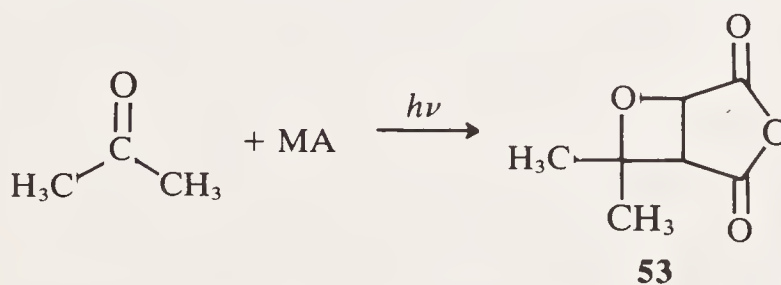


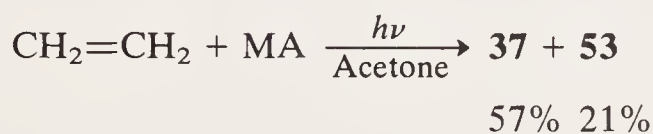
Fig. 6-4. Cyclobutene : bicyclopropyl ratios for the photosensitized addition of MA to acetylene ( $\circ$ ) and propyne ( $\Delta$ ) as a function of reciprocal MA concentration. From Reference 43.

#### 6.3.4. Miscellaneous Photoreactions

Ketones have been reported to undergo Paterno-Buchi<sup>(46)</sup> reactions with olefins to yield an oxetane derivative. MA also reacts with acetone to form the oxetane product **53** on irradiation.<sup>(47)</sup> Other ketones were also reported



to give the oxetane products. The oxetane **53** was also observed as a by-product during the photocycloaddition of ethylene to MA which was run in an acetone solution.<sup>(34)</sup>



The formation of oxetane from acetone and MA is complicated by dimerization of MA and polymerization.<sup>(6,47,48)</sup> Oikawa and Watanabe<sup>(48)</sup> have examined the structure of this white elastic polymeric material.

One of the interesting aspects of this reaction is its synthetic usefulness. Jones and Fantina<sup>(49)</sup> have studied the pyrolysis of the photoadducts of acetone

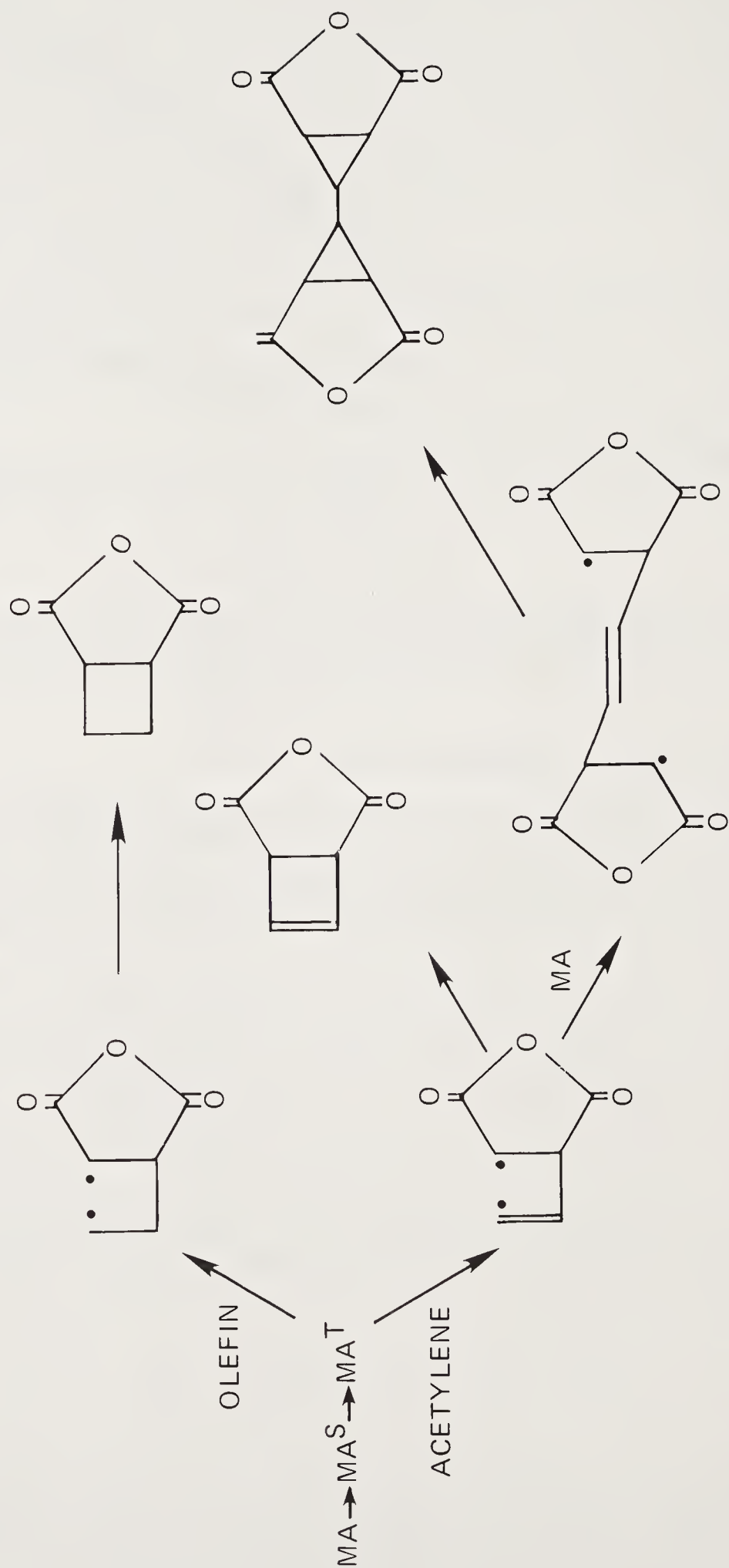
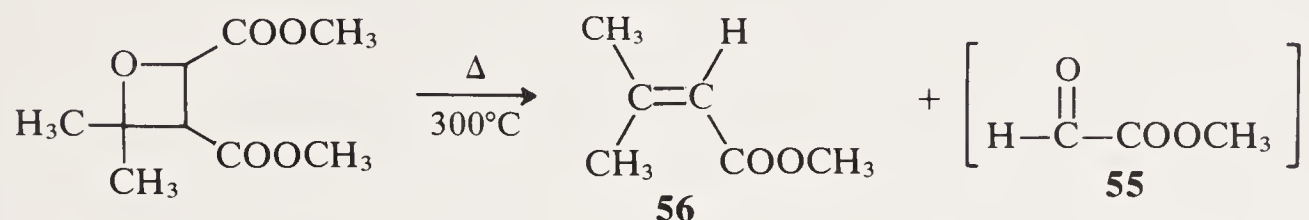


Fig. 6-5. General scheme for photoaddition of MA to simple olefins and acetylenes. From Reference 43.

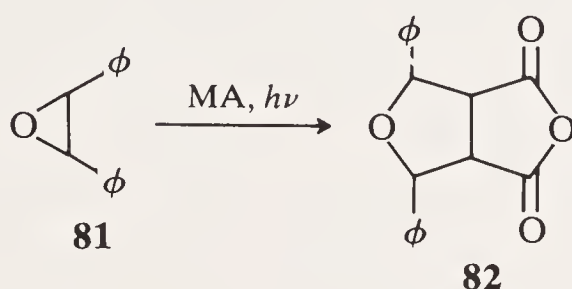


with MA, dimethyl maleate, and dimethyl fumarate. The MA adduct gave a complex mixture of products; on the other hand, the diester gave methathesis



products. Methyl glyoxalate **55** was unstable under the reaction conditions. However, a 90% yield of the butenoate **56** was observed. Thus, this could be an interesting approach to 2,2-disubstituted acrylates.

*Cis*- and *trans*-stilbene oxides **92** undergo photochemical ring opening due to a C—C bond scission. The resulting singlet or triplet state can be trapped with MA to yield the anhydride **93**. Geometric considerations for the product have been discussed.<sup>(82)</sup> A similar product is known to form on thermal reaction (see Chapter 7).



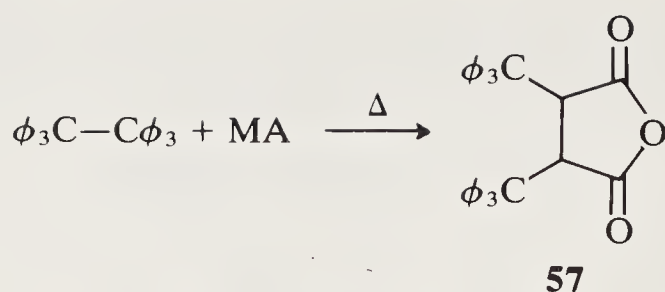
Thus, it appears that the photoreactions of MA have a wide range of synthetic usefulness which is far from exhausted.

#### 6.4. REACTIONS OF MA WITH FREE RADICALS

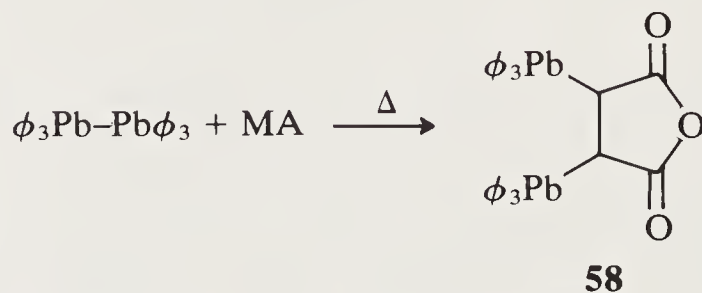
The reaction of MA with free radicals can find a place at a number of places in this book. Since during the radical-catalyzed polymerization such a process occurs, the major segment of these types of reactions are naturally covered in the polymerization section. However, above and beyond the polymer aspects of the reactions, some reactions are known which add radicals to the double bond of MA to give monomeric products. Since some of these radical generating processes have been photoinitiated, it is suitable to discuss them as a part of this section.

Conant and Chow,<sup>(50)</sup> on refluxing a benzene solution of hexaphenylethane and maleic anhydride, under N<sub>2</sub>, obtained a 25% yield of the adduct **57** (isolated as acid).

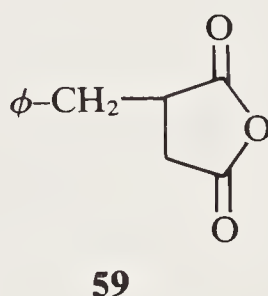
Triphenylmethyl radicals, which are viewed responsible for the product formation, are known to form upon heating of hexaphenylethane.



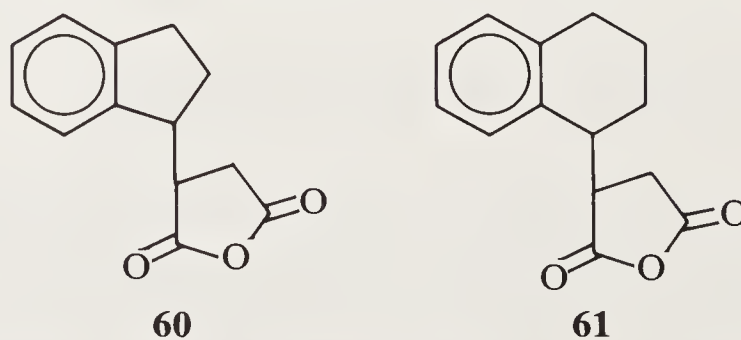
Hexaphenyllead has similarly been reported to add across the MA double bond.<sup>(51)</sup>



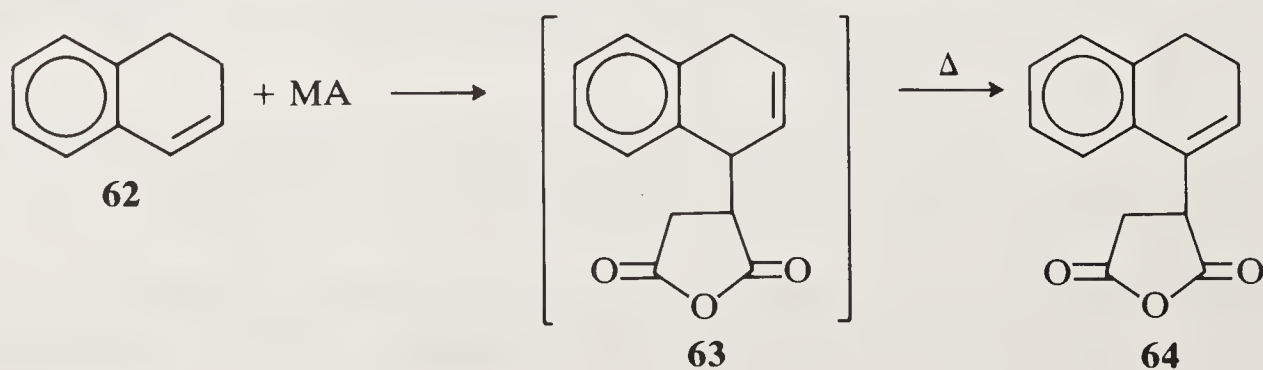
Binapfl obtained benzylsuccinic anhydride **59** on heating a solution of maleic anhydride in toluene at 305–315°C for 20 min.<sup>(39,52)</sup> The reaction was



reported to be catalyzed by I<sub>2</sub>, sulfur, copper-bronze, etc.<sup>(53)</sup> Alder and Wolff<sup>(54)</sup> also showed the production of **60** from indane and **61** from tetrahydronaphthalene on heating with MA at 250°C and I<sub>2</sub> catalyst.



1,2-Dihydronaphthalene **62** also was reported to yield **64**.<sup>(54)</sup> However, since the reaction was performed in the presence of an inhibitor, it is unlikely



that radicals are involved. It is possible that an ene reaction initially gave **63**, which on isomerization of the double bond yielded the product (see Chapter 5).

In a systematic study, Bickford and coworkers<sup>(55)</sup> later observed that the reaction of alkylaromatics with MA can be catalyzed by peroxides. Furthermore, they showed that the hydrogen alpha to the aromatic ring was necessary for the reaction, as shown by the lack of reaction with *t*-butylbenzene. Shecter and Barker<sup>(56)</sup> confirmed the radical nature of the process by demonstrating the inhibiting action of hydroquinone and the accelerating effect of a peroxide (Fig. 6-6) on the reaction of *p*-xylene with MA.

The data of Bickford *et al.*<sup>(55)</sup> are reported in Table 6.7. By the use of benzoyl peroxide, they showed that ethylbenzene gave the highest yield of the aralkylsuccinic anhydride. Shecter and Barker<sup>(56)</sup> also showed the generality of the reaction by reacting various substituted toluenes with di-*t*-butyl peroxide as initiator. Their data are shown in Table 6.8. No significant correlation was derived. The yield of the *o*-xylene adduct could be increased by higher dilution of MA. This and continuous formation of solid adducts (not characterized) was used to propose that the *o*-xylene radical could incorporate more than 1 mole of MA giving possible structures such as **65**.

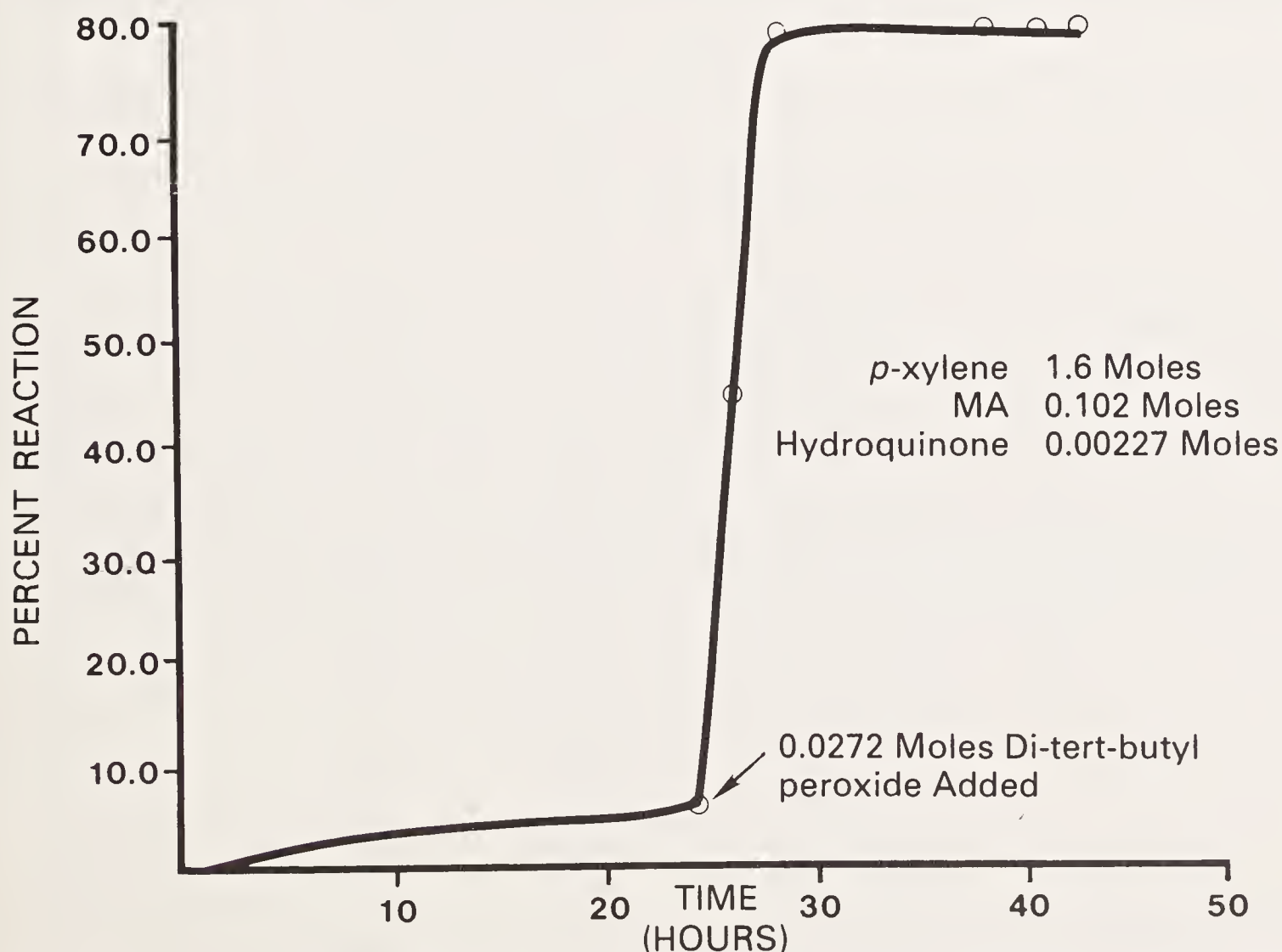
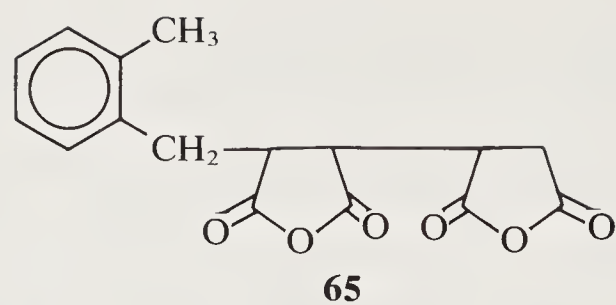


Fig. 6-6. Effects of hydroquinone and di-*tert*-butyl peroxide on reaction of *p*-xylene and MA at 150°C. [Reprinted with permission from *J. Org. Chem.* **21**, 1473 (1956). Copyright © 1956, American Chemical Society.]





Further investigations may prove interesting. Homopolymerization of MA has been examined using peroxide initiation<sup>(132,133)</sup> (see Chapter 8). Note that the yields of the adduct in Tables 6.7 and 6.8 are usually lower than would be obtained if all MA was selectively converted to the adducts. It appears, therefore, that homopolymerization may be the wasteful side reaction

Table 6.7. Reaction of Maleic Anhydride With Various Hydrocarbons<sup>a</sup>

Hydrocarbon	Benzoyl peroxide added (g)	Reaction time (h)	Maleic anhydride reacted (%)	Yield crude (%)
Toluene	5.0	0.0	0.0	38
		0.50	36	
		1.0	43	
		2.0	81	
		3.0	84	
Ethylbenzene	0.5	0.0	0.0	84
		0.25	38	
		0.50	67	
		1.0	91	
		2.0	92	
<i>p</i> -Xylene	2.0	0.0	0.0	70
		0.25	48	
		0.50	76	
		1.0	91	
		2.0	91	
Cumene	2.0	0.0	0.0	57
		0.25	57	
		0.50	78	
		1.0	91	
		2.0	90	
Cymene	0.3	0.0	0.0	72
		0.50	60	
		1.0	71	
		2.0	83	
		3.0	83	
<i>t</i> -Butylbenzene	1.0	0.0	0.0	0
		1.0	2	
		2.0	2	

<sup>a</sup> From Reference 55.

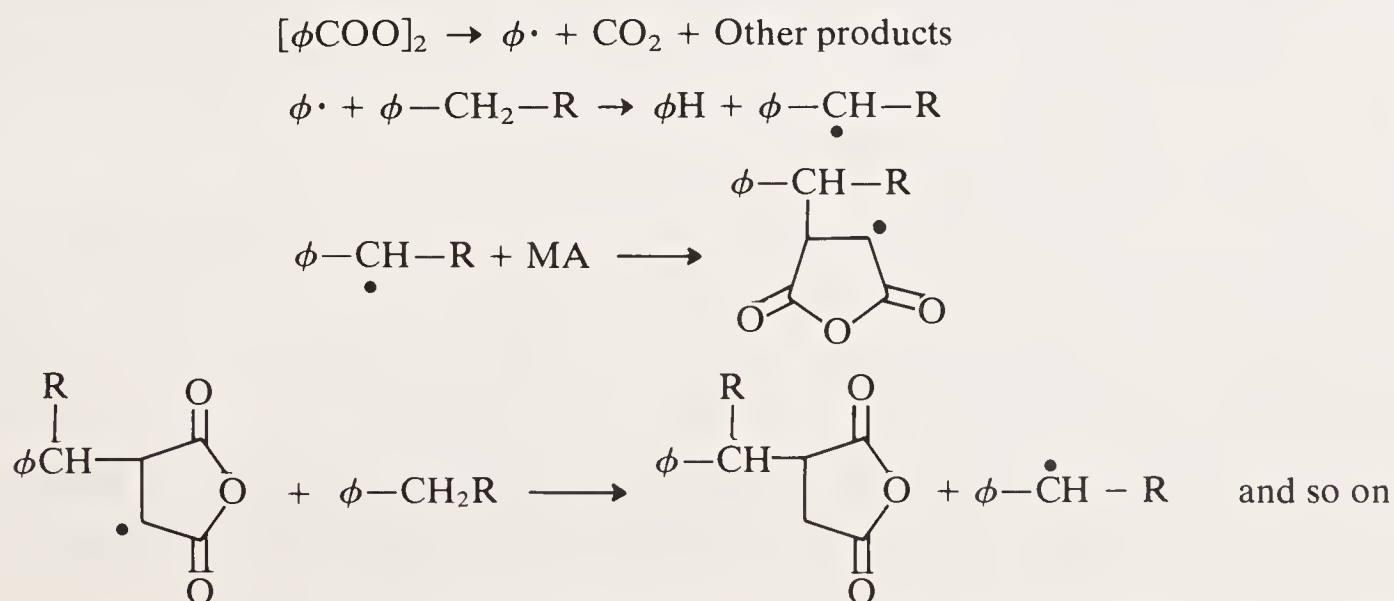
Table 6.8. Reaction of Maleic Anhydride with Substituted Alkylbenzenes<sup>a</sup>

Alkylbenzene	Product	Maleic anhydride reacted (%), 5 h	Yield (%)
<i>p</i> -Xylene	3-( <i>p</i> -Tolyl)-1,2-propanedicarboxylic acid	76	99
<i>m</i> -Xylene	3-( <i>m</i> -Tolyl)-1,2-propanedicarboxylic acid	73	79 (63)
<i>o</i> -Xylene	3-( <i>o</i> -Tolyl)-1,2-propanedicarboxylic acid	60	43
<i>p</i> -Chlorotoluene	3-( <i>p</i> -Chlorophenyl)-1,2-propanedicarboxylic acid	75	44 (30) (70)
<i>m</i> -Chlorotoluene	3-( <i>m</i> -Chlorophenyl)-1,2-propanedicarboxylic acid	—	39
<i>o</i> -chlorotoluene	3-( <i>o</i> -Chlorophenyl)-1,2-propanedicarboxylic acid	—	73
<i>p</i> -Methoxytoluene	3-( <i>p</i> -Methoxyphenyl)-1,2-propanedicarboxylic acid	72	38 (17)
<i>p</i> -Isopropyltoluene	3-Methyl-3-( <i>p</i> -tolyl)-1,2-butanedicarboxylic acid	85	89 (67)
<i>p</i> -Ethylisopropylbenzene	3-Methyl-3-( <i>p</i> -ethylphenyl)-1,2-butanedicarboxylic acid	88	99 (>51)
<i>p</i> -Ethyltoluene	3-( <i>p</i> -Tolyl)-1,2-butanedicarboxylic acid	85	65 (25)

<sup>a</sup> Reprinted with permission from *J. Org. Chem.* **21**, 1473 (1956). Copyright © 1956, American Chemical Society.

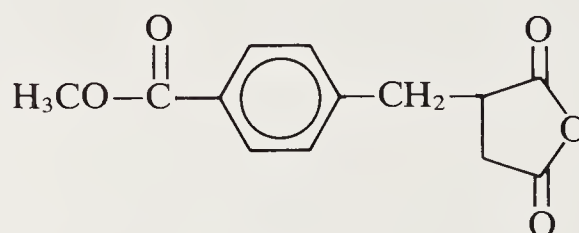
consuming MA. In Table 6.8, good to excellent yields are also reported for *p*-isopropyl-toluene (*p*-cymene), *p*-ethylisopropyl-benzene, and *p*-ethyl-toluene. In each case, the adduct was derived from the reaction at the most substituted *alpha*-carbon. This is in general accord with the relative stabilities of the corresponding radicals, i.e., primary < secondary < tertiary.

The above evidence is thus in agreement with the radical mechanisms of the reaction proposed by Bickford *et al.*<sup>(55)</sup> which is shown in the scheme below:

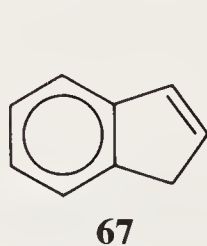
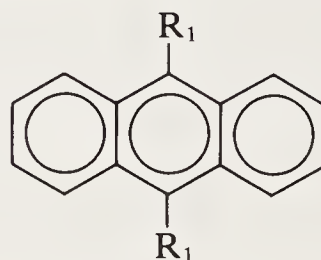


Shecter and Barker<sup>(56)</sup> reported that the reaction of *m*- and *p*-xylenes was first order in MA concentration up to 60% reaction. The chain length of 160–180 for *p*-xylene and 75–105 for *m*-xylene was also reported. *p*-Cyanotoluene did not react.

The reaction is quite general as can be seen from the various reactions. Isopropyl-naphthalene<sup>(57)</sup> has been reported to add across the MA double bond. Methyl-*p*-toluate similarly adds, producing a unique tri-acid derivative **66**.<sup>(58)</sup>

**66**

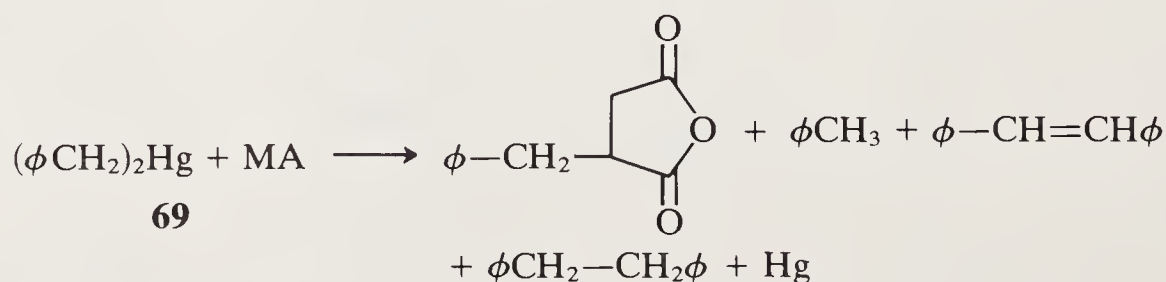
The presence of hydrogen alpha to the aromatic ring is necessary, as mentioned above, but not sufficient. For example, it may be recalled that indene **67**, which has benzylic hydrogens, gives a Diels–Alder reaction product.<sup>(59)</sup> Similarly, 9-methylantracene **68a** and 9,10-dimethylantracene **68b** also give the products corresponding to the [4 + 2] cycloaddition.<sup>(60)</sup>

**67**

**68a**  $R_1 = \text{CH}_3, R_2 = \text{H}$   
**68b**  $R_1 = R_2 = \text{CH}_3$

MA adducts of alkylaromatics have potential as monomers. Stevens<sup>(61)</sup> claims chemical resistance of unsaturated polyesters when they contain adducts made from MA with toluene, *p*-xylene, ethylbenzene, and cumene. The adducts have also been proposed as intermediates for plasticizers, synthetic resins,<sup>(62)</sup> and dye intermediates.<sup>(63)</sup>

Benzyl radicals have also been proposed in the reaction of dibenzylmercury **69** with MA. When a 1:1 mixture of the two was heated at 100°C for

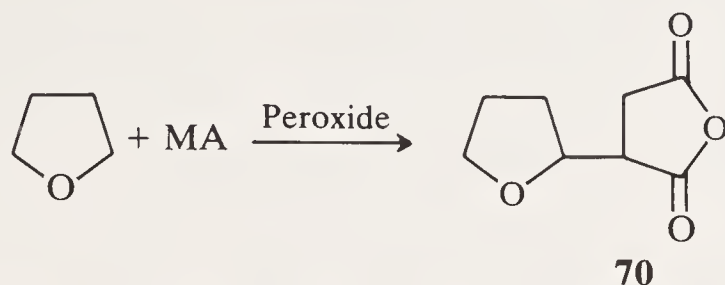


10 min under nitrogen; a rapid exothermic reaction occurred.<sup>(64)</sup> Of the benzyl groups, 22% were observed as benzylsuccinic anhydride; dibenzyl, stilbene,

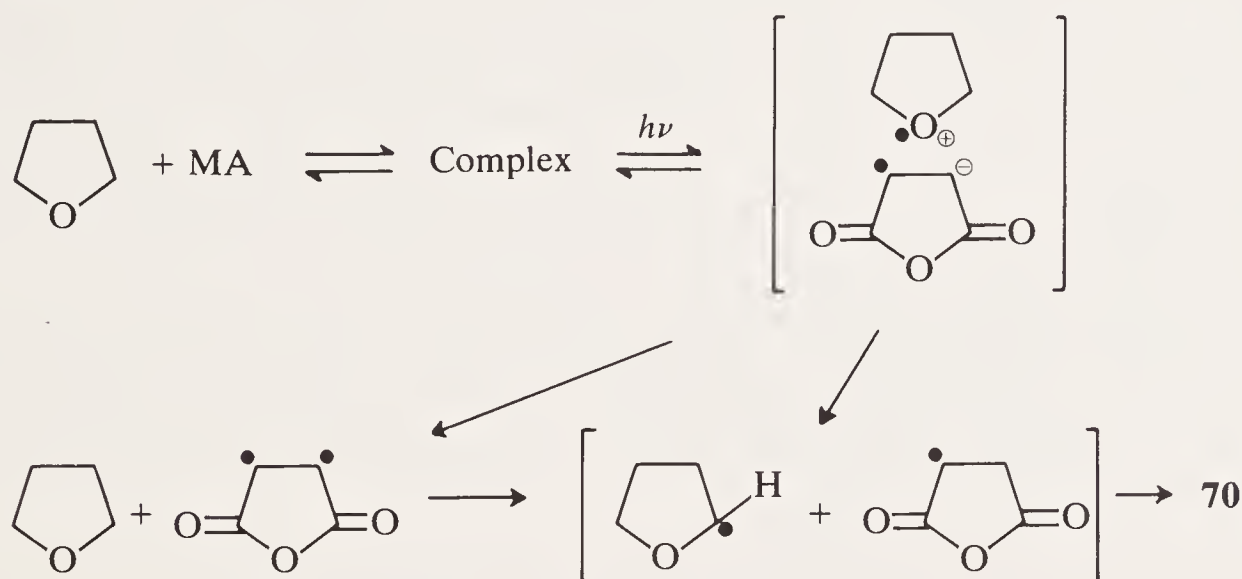


and toluene were other products. A yellow-colored complex that formed on mixing the two reactants was suggested as an intermediate. In the absence of another hydrogen source, the benzyl radical provides the hydrogen atom, subsequently yielding a carbene. The latter dimerizes to stilbene.

A radical generated from THF can be added across MA. Jacobs and Ecke<sup>(65)</sup> obtained a 70% yield of the (tetrahydro-2-furyl)-succinic anhydride **70** during a peroxide-induced reaction of the THF with MA.

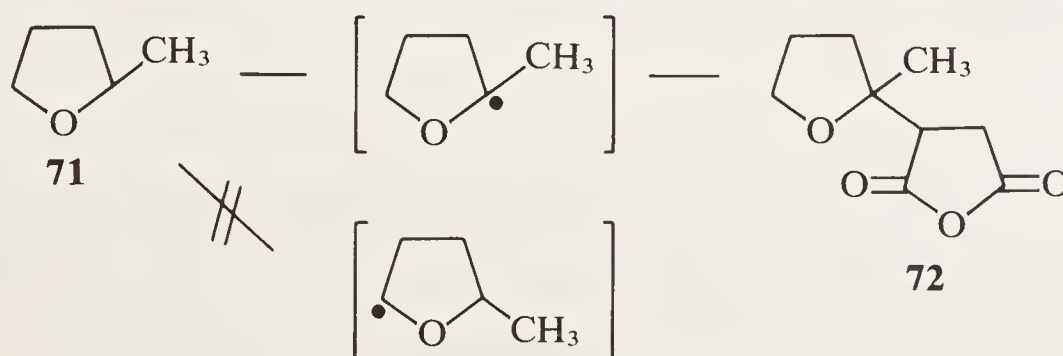


Ledwith and Sambhi<sup>(66)</sup> observed a similar reaction on exposing a solution of MA in THF to UV or sunlight. They proposed that the excited charge-transfer complex was responsible for the reaction. The following scheme was proposed.



Although THF and MA do form a charge-transfer complex, no definitive evidence for the intermediacy of the latter was given.

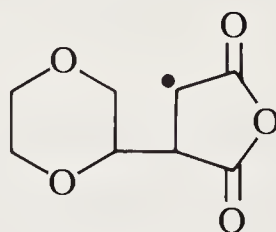
When tetrahydro-2-methylfuran **71** was used, the product was (tetrahydro-2-methyl-2-furyl)-succinic anhydride **72**. This suggests that the tertiary radical is the most favored species formed.<sup>(65)</sup> The reactions were claimed to be specific for five-membered cyclic ethers since tetrahydropyran



and 1,4-dioxane failed to yield any distillable product. Krejki and Pichler<sup>(76)</sup> have studied the reaction of cyclic ethers with MA using various means of initiation. It was observed that benzoyl peroxide initiation succeeded with THF only. Reaction was obtained with THF, 2,5-dihydropyran, and 1,3-dioxolane when UV initiation was used. In order to prepare adducts from 1,4-dioxane, initiation by  $\gamma$  rays was necessary. Based on this experience, the following order of reactivity by  $\gamma$ -ray initiation was given:



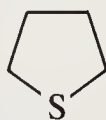
Kasperski and coworkers<sup>(79)</sup> have recently obtained evidence for radical **73** on UV irradiation of MA solution in 1,4-dioxane.



73

It is noteworthy that azobisisobutyronitrile (AIBN) catalyzed homopolymerization of MA was fastest in 1,4-dioxane among a number of cyclic ethers studied.<sup>(134)</sup> Thus, polymerization may be an important side reaction which can explain the poor addition of 1,4-dioxane. Efforts such as high MA dilution or slow additions of initiator and MA appear worth undertaking for higher yields of these interesting products.

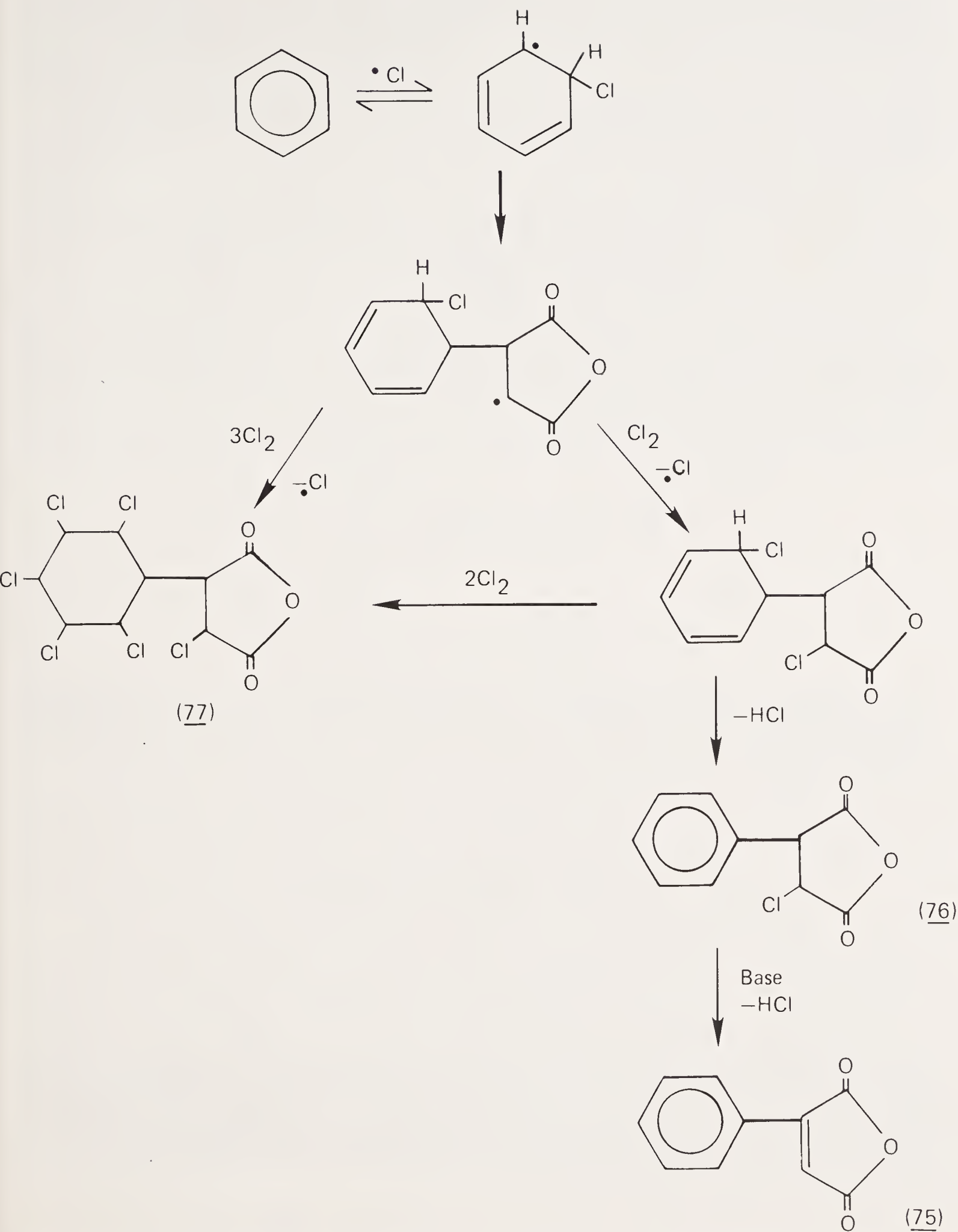
Tetrahydrothiophene **74**, on the other hand, reacted with MA only with AIBN as an initiator. Benzoyl peroxide failed to yield any product. Jacobs and Ecke<sup>(65)</sup> described the product as a 1 : 1 adduct so the structure is probably similar to the THF adduct **70**.



74

Ecke *et al.*<sup>(67,68)</sup> have demonstrated a method of forming phenylmaleic anhydride **75** in low yields in two steps. On photochlorination of maleic anhydride in benzene, an 18% yield of  $\alpha$ -chloro- $\alpha'$ -phenylsuccinic anhydride **76** was formed. The other major product was **77**. Compound **76** could be dehydrohalogenated to **75** in a 79% yield. From the dependence of chlorination on peroxide or light initiation and the observation that the reaction is inhibited by  $\text{O}_2$ , it was concluded that the reaction occurs via a free-radical pathway. The overall scheme for various products is shown in Fig. 6-7.

It is interesting that Ecke *et al.*<sup>(67,68)</sup> mentioned other compounds, e.g., chlorobenzene, benzotrichloride, methyl benzoate, and toluene, also giving reaction; however, no details were mentioned. Furthermore, the reaction of

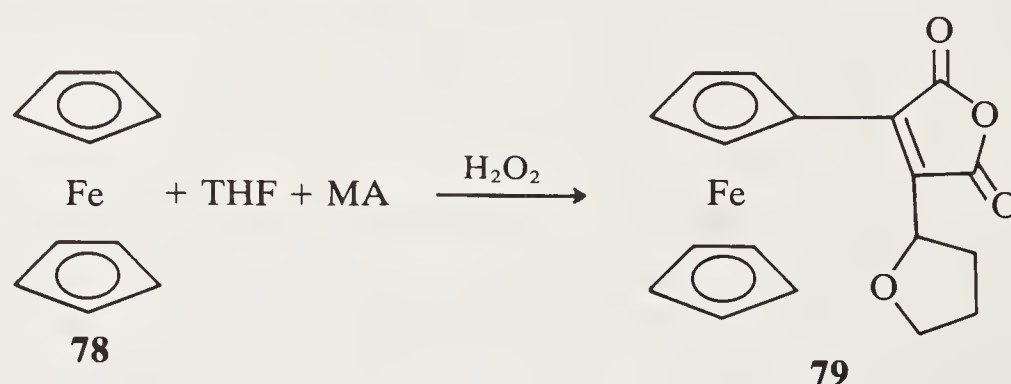


**Fig. 6-7.** Reaction scheme for photochlorination of MA in benzene. [Reprinted with permission from *J. Am. Chem. Soc.* **78**, 79 (1956). Copyright © 1956, American Chemical Society.]

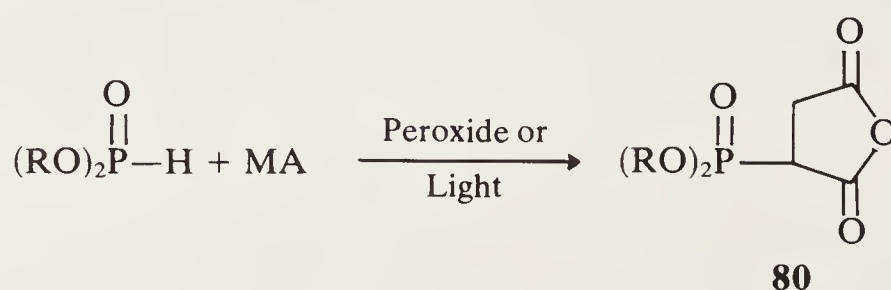


toluene was reported to be unusual in that no benzylchloro-succinic anhydride was reported—which may be expected considering the radical nature of the process. Actually a tolyl derivative was mentioned. When bromine was used in place of chlorine, no reaction occurred with benzene and maleic anhydride. Thus, there are some definitely intriguing aspects of this chemistry that closer examination may answer.

An unusual radical reaction of MA with ferrocene **78** in THF was reported by Bozak.<sup>(69)</sup> In a  $\text{H}_2\text{O}_2$  initiated reaction, a small amount of product **79** was obtained at room temperature. No other products were mentioned. The structure **79** was assigned on the basis of elemental and spectroscopic analysis. No reaction occurred in the absence of  $\text{H}_2\text{O}_2$ , and so a radical reaction was proposed. No detailed mechanism for the formation of **79**, which still has the intact olefin bond, was proposed.

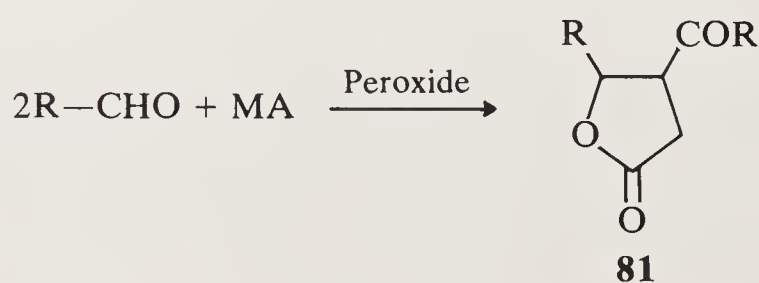


Peroxide-catalyzed addition or organophosphorus compounds with at least one P–H bond<sup>(70)</sup> has been reported. The reaction can also be initiated by UV radiation.



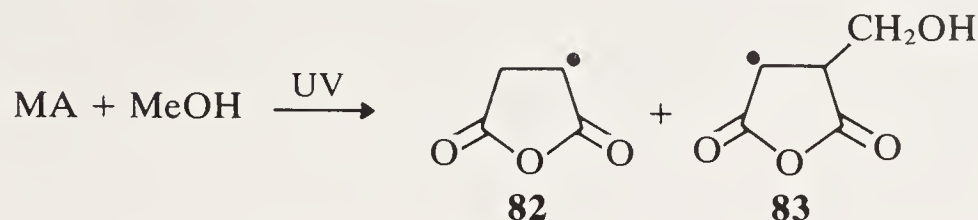
$\text{R} = n\text{-butyl, ethyl, 2-ethylhexyl, etc.}$

This interesting reaction and particularly its products do not appear to have been explored much. The products such as **80** were claimed to be useful as hydraulic fluids, heat transfer media, plasticizers, lubricating oil additives, antirust agents, and in ore floatation.<sup>(70)</sup>

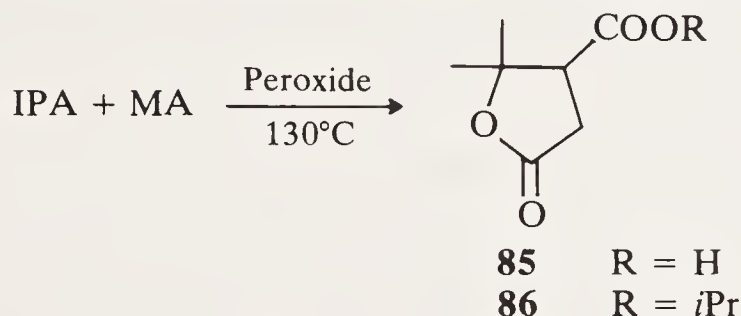


Aldehydes have also been reported to add under radical initiation. For example, on refluxing a mixture of MA, *n*-butyraldehyde, and benzoyl peroxide, one obtains a lactone **81** ( $R = n\text{-C}_3\text{H}_7$ ).<sup>(83)</sup> Other normal aldehydes from  $\text{C}_5$  to  $\text{C}_8$  could also be used.

An ESR study of the UV reaction of methanol with MA at low temperatures gave evidences of the following species according to Hellebrand *et al.*<sup>(71,72)</sup>



Of course, it is known that the radical produced by abstraction of an  $\alpha$ -hydrogen from alcohols can add to the olefin in a chain process.<sup>(73,74)</sup> Recently, Fukunishi *et al.*<sup>(75)</sup> have examined radical-catalyzed alcohol addition to MA and its esters. A high yield of terebinic acid **85** and its isopropyl ester **86** was



obtained during the peroxide-catalyzed reaction of isopropyl alcohol with MA. Similar lactones were also obtained from dialkyl maleate and fumarate.

Electrolytic reduction of maleic and fumaric derivatives leads to dimerization to produce a tetracarboxylic acid product.<sup>(145)</sup> The process occurs through the intermediacy of a radical anion. The latter can be carboxylated in the presence of  $\text{CO}_2$ . The tetracarboxylic acid derivatives have been proposed for semipermeable polyimide membranes.<sup>(146)</sup>

Thus, there are several maleic anhydride derivatives that can be obtained through radical-initiated reaction. Alkyl radicals are shown to react with MA much faster than methylmaleic anhydride.<sup>(119)</sup> The initiation may be obtained with peroxide, AIBN, or, in some cases, light. It would be difficult to assess the importance of MA's radical reaction without including the homo and copolymerization aspects, which are included elsewhere in the book. Suffice it to say that these two aspects may contribute to formation of undesired by-products and could potentially be prevented or curtailed significantly.

## 6.5. COMPLEXES OF MA

The term "complex" has been used to describe products of two reactants resulting from interactions distributed over a strength spectrum spanning very



strong and very weak. In organometallic chemistry, complexes of MA are formed that can be isolated and characterized. In other cases, complexes are inferred from spectroscopic properties of a solution of MA with other species. It may be of interest to note that MA, due to its variety of reactive sites, can function as a donor or an acceptor. As a donor, it can interact at one of three sites; namely, the olefin bond, carbonyl oxygen, or anhydride oxygen. The  $\pi$ -electron system of MA acts as an acceptor. In spite of its complexity, possible mechanistic information can be obtained—for some systems. In Sec. 6.5.1, a brief discussion of MA complexes involving charge-transfer, MA as a base, and with transition metals is given.

### 6.5.1. Charge-Transfer Complexes

In many reactions of MA, e.g., photochemical, radical, Diels–Alder, and polymerizations, the intermediacy of a charge-transfer (CT) complex is invoked. By this is meant rapid and reversible interaction of two molecules in solution, the presence of which could be detected by the appearance of a broad intense band in the visible or ultraviolet absorption spectrum at wavelengths longer than those due to the individual components. In other words, this definition really defines “complexes showing charge-transfer absorption.”<sup>(84)</sup> This method-limited definition could be misleading. For example, we also know that in some cases complexes may be inferred; e.g., in case of MA:acetone, but no distinct UV or visible absorption may be observed.<sup>(85–87)</sup> Mulliken<sup>(88)</sup> has used the term “electron donor–acceptor (EDA) complexes.”

From the standpoint of an experimental chemist, a CT complex (or EDA complex) involves an integral ratio of donor and acceptor components. Enthalpy of formation is usually a few calories or less. More importantly, the rates of formation and decomposition are so high that by normal techniques of measurement, the process may be called instantaneous. The electron affinity of MA as a CT acceptor has been determined to be  $1.33 \pm 0.13$  eV.<sup>(137)</sup>

### 6.5.2. Detection of CT (EDA) Complexes—Physical Methods

A rapid visual color change upon the mixing of components has been regarded as an evidence of complex formation.<sup>(117)</sup> However, so far, for the study of CT complexes UV–visible spectroscopy is most widely employed. In Fig. 6-8, absorption curves for MA in chloroform and MA in benzene are given along with that of neat benzene. As is evident, a longer wavelength band with high intensity is observed and is ascribed to the CT complex.<sup>(22)</sup>

A number of workers have studied the absorption maxima by spectroscopic measurements (see Table 6.9). It may be added that often two or more maxima may be observed. For the interpretation of these data, the original



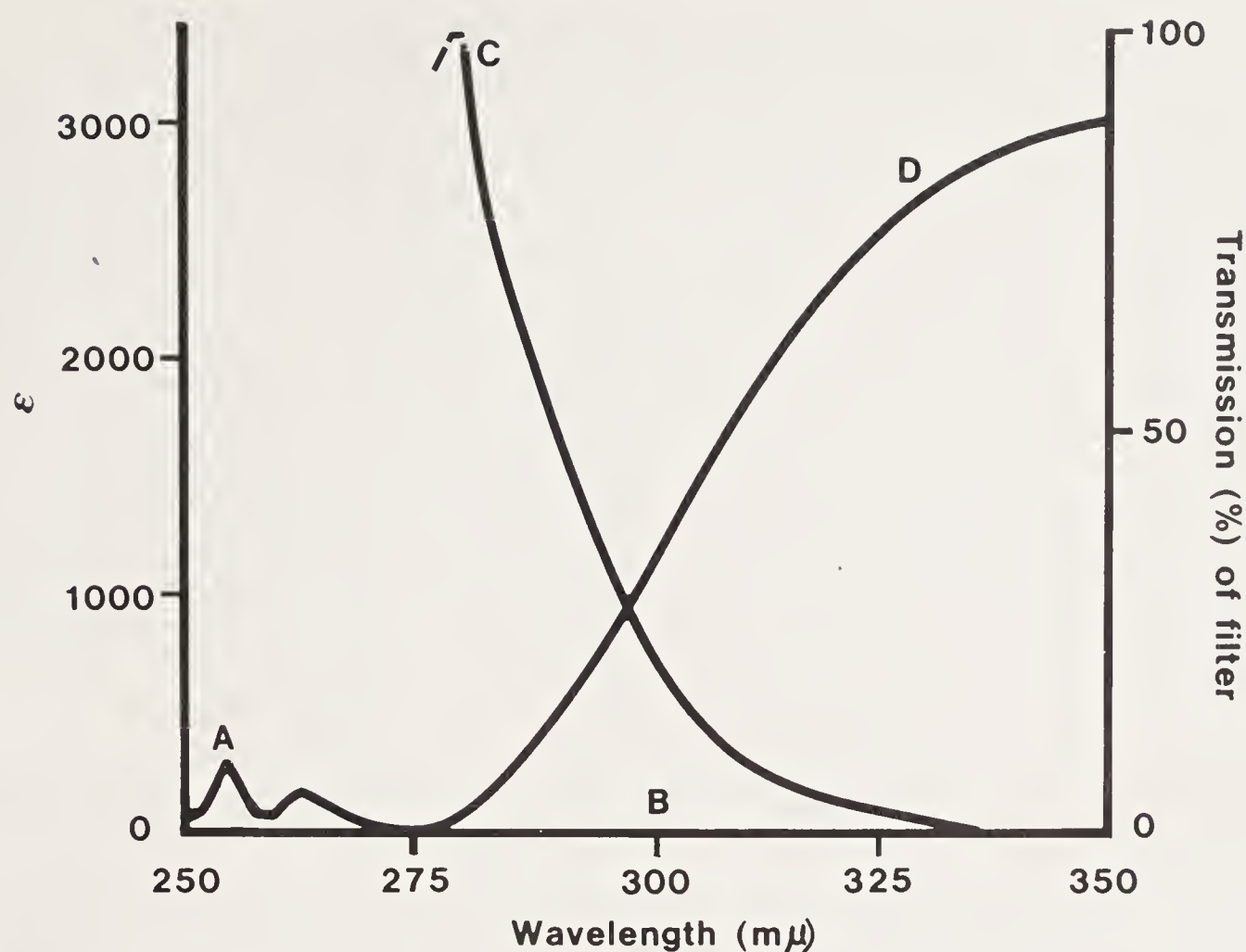


Fig. 6-8. Absorption curves of (A) benzene, (B) maleic anhydride (in chloroform), and (C) the benzene-MA charge-transfer complex. (D) Transmission curves for the filter. From Reference 22.

articles and reviews<sup>(84,89,90)</sup> are recommended. Complexes of benzene, substituted benzene, polycyclic hydrocarbons, heterocyclic ethers, sulfides, amines, and olefins are included as representative cases. In some cases, spectra have been recorded with a solvent present. In others, the donor is used as a solvent as Bryce-Smith *et al.*<sup>(90)</sup> have done by employing a very-thin-film technique.

In addition, nuclear magnetic resonance (NMR) and infrared methods have been widely used. For example, the chemical shift of MA in benzene or acetone is concentration as well as temperature dependent. Silber *et al.*<sup>(85)</sup> have thus determined equilibrium constants for the complexes. Also used successfully is analytical calorimetry. In Tables 6.10 and 6.11 are shown data for MA-benzene and MA-acetone complexes, respectively. Comparisons with those results from NMR studies are given. Obviously good correlations are obtained. Based on their data, 25% of MA (0.044 mole fraction) in benzene is present as complex whereas that number is 55% for MA (0.25 mole fraction) in acetone.<sup>(140)</sup>

The quantitative analysis also involves various methods to determine equilibrium positions. All the methods mentioned above and others, such as dielectric constant measurements and osmometry, have been used. The interested reader is referred to an excellent book by Foster.<sup>(84)</sup>

Table 6.9. Charge-Transfer Complexes of MA

Donor	$\lambda_{\text{max}}$ (m $\mu$ )	Remarks	References
Benzene	268		90, 92
Toluene	278		90, 92
Ethylbenzene	274		90
Cumene	274		90
<i>t</i> -Butylbenzene	280		90
<i>o</i> -Xylene	271		90
<i>p</i> -Xylene	285		90
Mesitylene	296	CHCl <sub>3</sub> solvent	92
Durene	315	CHCl <sub>3</sub> solvent	90
Hexamethylbenzene	~345	CHCl <sub>3</sub> solvent	90, 92
Naphthalene	325	CHCl <sub>3</sub> solvent	91
Phenanthrene	354	CHCl <sub>3</sub> solvent	91
Chrysene	367	CHCl <sub>3</sub> solvent	91
Pyrene	384	CHCl <sub>3</sub> solvent	91
Anthracene	392	CHCl <sub>3</sub> solvent	91, 92
Cyclohexene	270 (~293)		32
2-Butyne	~230		32
Neohexene	~245		32
Styrene			92
Allyl chloride			92
Anisole			92
Dimethylaniline			92
Thiophene	270		32
Furan	292		32
<i>N</i> -Methylpyrrole	345		32
Diazabicyclooctane	317		93
Acenaphthene			93
2,3-Dihydrothiophene	355	CHCl <sub>3</sub> solvent	94
2,3-Dihydrothiopyran	348	CHCl <sub>3</sub> solvent	94
<i>p</i> -Dithiene	382	CHCl <sub>3</sub> solvent	94
Phenylvinyl sulfide	360–390	CHCl <sub>3</sub> solvent	94
Ethylvinyl sulfide	360–390	CHCl <sub>3</sub> solvent	94

Table 6.10. Maleic Anhydride–Benzene Molecular Complex

Result <sup>b</sup>	Experimental method	Correlation coefficient
$K = 2.13$ mol/fraction	NMR (39.8°C)	0.995
$\Delta H = -4.2$ kcal/mol	Heats of solution (39.8°C)	-0.999
$\Delta S = -11.7$ cal/mol K	van't Hoff equation	—
$\Delta c = -118.2$ Hz	NMR (39.8°C)	0.995

<sup>a</sup> From Reference 85.  
<sup>b</sup> 1 cal = 4.184 J.

Table 6.11. Maleic Anhydride–Acetone Molecular Complex

Result <sup>b</sup>	Experimental method	Correlation coefficient
$K = 1.37$ mol/fraction	NMR (39.8°C)	0.992
$K = 1.58$ mol/fraction	Heats of dilution (25.0°C)	0.999
$\Delta H = -3.2$ kcal/mol	NMR (temperature variation)	0.959
$\Delta S = -9.9$ cal/mol K	van't Hoff equation	—
$\Delta H = -3.63$ kcal/mol	Heats of dilution (25.0°C)	0.999
$\Delta H = -3.73$ kcal/mol	Heats of solution (25.0°C)	-0.999
$\Delta S = -11.3$ cal/mol K	van't Hoff equation	—
$\Delta c = +48.0$ Hz	NMR (39.8°C)	0.992

<sup>a</sup> From Reference 85.  
<sup>b</sup> 1 cal = 4.184 J.

6.5.3. Detection of CT Complexes—Polymerization

Since the 1940s, it has been recognized that MA forms alternating copolymers with various olefinic monomers such as styrene,<sup>(96,97)</sup> allyl acetate,<sup>(96)</sup> and *p*-dioxene.<sup>(98)</sup> Recently, dienes,<sup>(99,100)</sup> furan<sup>(101,102)</sup> *N*-vinyl compounds,<sup>(141)</sup> and unsaturated sulfides<sup>(95)</sup> have also been added to this list.

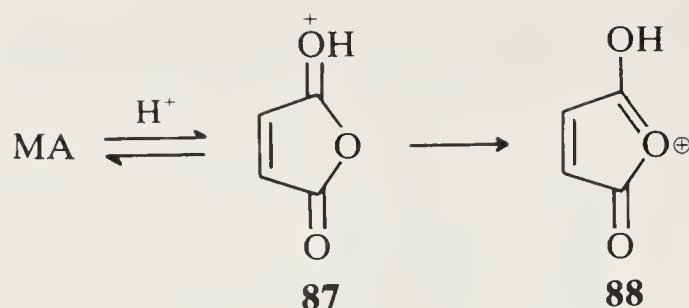
It has been proposed that this perfectly alternating character of the polymer, no matter what the concentration of the individual components, may mean that polymerization is of the complexes. The mechanism has been discussed by Ratzsch.<sup>(103)</sup> Furthermore, Tamura *et al.*<sup>(142)</sup> have described the polymerization of MA:amide complexes with methyl methacrylate. (See Chapter 10 for the discussion on charge-transfer polymers.)

When rationalizing a reaction as involving charge-transfer intermediates, caution should be exercised. Complex formation and its slow disappearance during the reactions may result from side reactions and/or disappearance of one of the components, leading to unwarranted conclusions.

6.5.4. MA with Acids

Leisten<sup>(104)</sup> has shown that MA can be protonated in very strong acids such as sulfuric. Olah and coworkers<sup>(105)</sup> have studied the interaction of MA with magic acid (FSO<sub>3</sub>H–SbF<sub>5</sub>) in liquid sulfur dioxide by nuclear magnetic resonance spectroscopy. They found that on dissolving MA in 0.5 equivalent (1:1) magic acid in SO<sub>2</sub> solution, vinylic hydrogens were deshielded (from  $\delta$ 6.83 to 7.21 ppm). They also observed a very deshielded proton at  $\delta$ 14.5 which was assigned to the –OH proton of protonated MA **87**. As the strength of acid is increased, intermolecular proton exchange and further protonation may be brought about.





Paul *et al.*<sup>(106)</sup> have studied the basicities of some anhydrides in fluorosulfuric acid ( $\text{FSO}_3\text{H}$ ), disulfuric acid ( $\text{H}_2\text{S}_2\text{O}_7$ ), and sulfuric acid. The dissociation constants determined by conductivity measurements are shown in Table 6.12. All anhydrides studied were weakly basic with strong acids such as fluorosulfuric and sulfuric. Lower basicities of cyclic anhydrides have been interpreted as arising from the resistance to delocalization of positive charge as illustrated with MA as an example in **87**  $\rightleftharpoons$  **88**.<sup>(107)</sup> This lowers the sensitivity of MA hydrolysis to perchloric acid catalysis.

Lewis acids, such as aluminum chloride, boron trifluoride, and zinc chloride, also react with MA. Complexes like MA:2 acceptor are proposed to be intermediates for Friedel–Crafts acylation reactions.<sup>(108,118)</sup> Some of these complexes have been identified by spectroscopic methods.

#### 6.5.5. MA with Transition Metals

MA is capable of donating electrons from the olefin  $\pi$  bond like other olefins. Besides transitory equilibrium species proposed as intermediates during various addition reactions of the olefin, the  $\text{C}=\text{C}$  double bond can function as a ligand. In so doing, it leads to a variety of transition-metal complexes. Weiss and Stark<sup>(109)</sup> obtained bis-(maleic anhydride)nickel (O) as orange crystals when a benzene solution of MA and nickel carbonyl was heated.



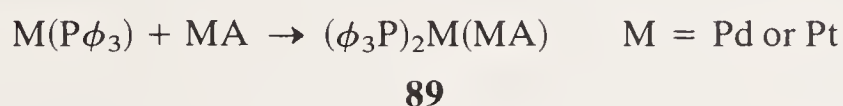
Complexes of other metals such as iron, of the type  $(\text{MA})\text{Fe(CO)}_4$  have been reported<sup>(110,111,120)</sup>; so have those of chromium and manganese,<sup>(111)</sup> of the type  $(\text{Ar})\text{M(CO)}_2(\text{MA})$  where M is chromium or manganese.

Table 6.12. Dissociation Constants of Acid Anhydrides in  $\text{HSO}_3\text{F}^a$

Compound	$K_b \times 10^2$ $\text{HSO}_3\text{F}$	$K_b \times 10^2$ $\text{H}_2\text{S}_2\text{O}_7$	$K_b \times 10^2$ $\text{H}_2\text{SO}_4$
Phthalic anhydride	24.56	Fully ionized	15.86
Monochloroacetic anhydride	32.88	Fully ionized	20.56
Maleic anhydride	54.92	78.86	38.96
Succinic anhydride	54.92	88.08	36.72

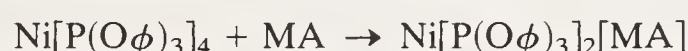
<sup>a</sup> From Reference 106.

Palladium and platinum complexes of MA can also be prepared by ligand substitution. Takahashi and Hagihara<sup>(112)</sup> observed that on treatment with a THF solution of tetrakis(triphenylphosphine) metal, MA gave complexes such as **89** (metal = Pd or Pt). Yields were 88–99%.



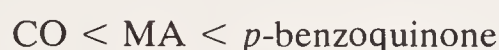
Cenini *et al.*<sup>(113)</sup> have obtained the complex **89** (M = Pt) by exchanging MA with the corresponding ethylene complex. Takahashi *et al.*<sup>(114)</sup> have utilized the palladium complex **89** (M = Pd) as a catalyst for linear dimerization of butadiene.

Bamford and Hughes<sup>(115)</sup> observed a reversible reaction on treatment of MA with tetrakis(triphenylphosphite)nickel.



Interestingly, if this reaction were allowed to run in the presence of a monomer such as methyl methacrylate or styrene, polymerization of the monomer occurred, suggesting the presence of radical species.

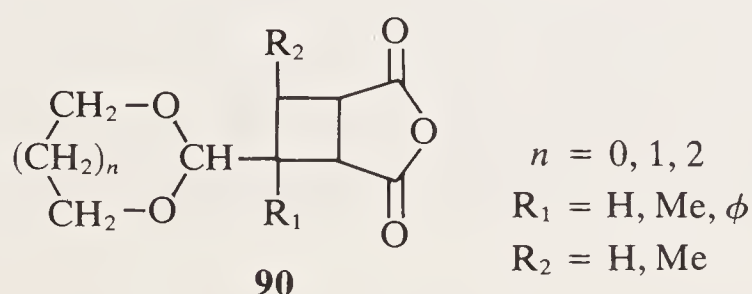
MA as a ligand is an acceptor or a  $\pi$ -acid ligand. Here, from a study of complexes of Cr, Mo, and W, the following acceptor activity order has been given<sup>(116)</sup>:



Study of MA complexes of transition metals is a growing field. It has many possibilities in addition to catalysis still unrealized. A section like this is meant to hint at this reactivity of MA rather than cover its present scope.

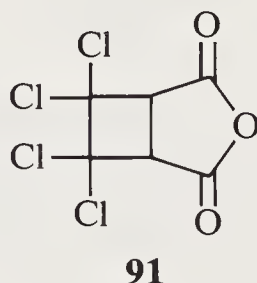
## 6.6. EPILOGUE

The last 20 years have seen a series of investigations involving photochemical reactions of MA. It was also observed that some of these products were obtainable by radical initiations and such information has led to understanding of the processes involved. The new molecules produced can have a variety of applications such as epoxy-curing agents, as cross linking anhydrides, as well as intermediates.<sup>(55,61,122–124)</sup> A Soviet patent suggests photoadducts **90** made from the acetal of acrolein or the like as filler for bitumen electrical insulation.<sup>(126)</sup>





Boule *et al.*<sup>(121)</sup> have mentioned the formation of photoadduct **91** by the reaction of tetrachloroethylene with MA. This product contains 53.76% Cl by weight and may be a reasonable alternative to chlorendic anhydride as a fire-retardant monomer. Adducts of other halogenated olefins hold similar possibility.



Furthermore, potential of some of these cyclic products as intermediates in the agricultural field are untested. Photochemical addition of MA to polymers such as polystyrene<sup>(129)</sup> may provide unique properties. However, development of these reactions is slow in coming, particularly so for the photochemical reactions. The biggest problems plaguing these potentially interesting products are:

- low yields of the desired products
- long reaction times needed for high yields
- overall inefficiency of some processes

Thus, a 93% yield of **1** may be obtained after 78 h of direct sunlight.<sup>(123)</sup> However, it should be remembered that industrial photochemistry is still in its infancy. It is encouraging that recently, the chemical industry has felt some comfort with it.<sup>(127,128)</sup> Furthermore, photocuring of coatings is beginning to gain popularity and Toray's caprolactam process has shown that photochemistry may not be restricted to the reaction of pharmaceutical and specialty industries. Thus, as the external limitations of photochemistry are gradually disappearing, it is expected that the internal limitations mentioned above will be understood and tackled in the future.

Radical addition to MA is a basic process involving radical polymerization involving MA. However, we examined a variety of products that may lead to intermediates and monomers having unusual properties.<sup>(61-63,67,68,70)</sup> A vast array of reagents may thus be added to MA. These reactions are worth understanding so that the products may be exploited to their full potential.

Complexes of MA have shed considerable light on the understanding of the mechanism of MA reactions. Particularly, metal complexation may allow reactions of MA by protecting the olefin function during the reaction. Preparation of maleanilic acid by this approach has been reported<sup>(144)</sup> in high yields. Maleimide formation by protecting the geometry may be possible. These and other possibilities make MA such an interesting molecule to work with.



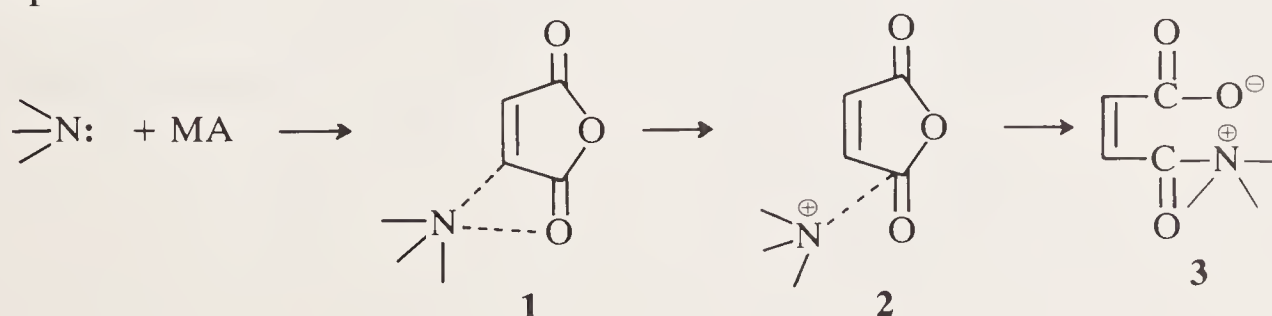
# UNUSUAL REACTIONS

## 7.1. INTRODUCTION

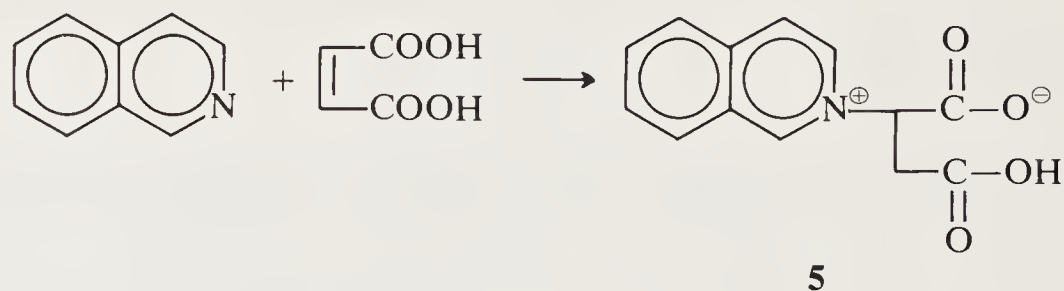
The purpose of this chapter is to introduce a number of useful synthetic reactions. Admittedly, all of these reactions are not unusual in the sense of organic chemistry and a few would have been predicted. However, some are unusual in the sense that they involve both the functional groups of MA. In some cases the ring system is unique for the reaction, for example, in the oxauracil synthesis. Also included in this chapter are 1,3-dipolar cycloadditions. Here too, some cases are given where more than one molecule of MA participates to arrive at quite unusual products. Some of these reactions are very high yielding and they are too useful synthetically to be regarded as extraneous. We believe Sec. 7.2 will justify these comments.

## 7.2. REACTIONS WITH AMINES

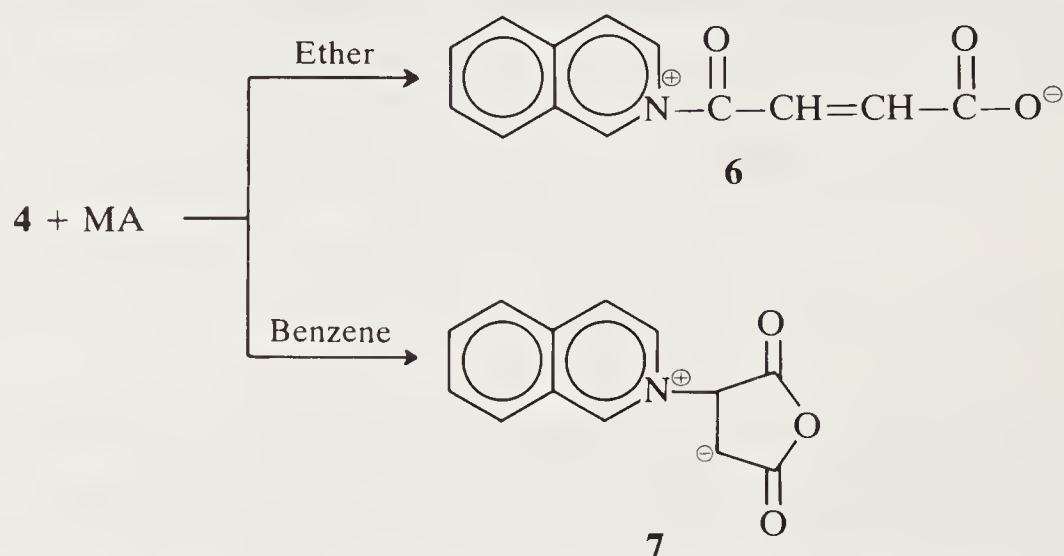
Tertiary amines, unlike their phosphine analogues, enter into a variety of reactions depending upon their overall structure. Van Alphen<sup>(1)</sup> examined the reaction of triethylamine with MA. An impure black substance was isolated which was soluble in water and released triethylamine on treatment with alkali. Mayahi and El-Bermani<sup>(2)</sup> have observed a very exothermic reaction on mixing the same reactants neat. However, they also observed a clear yellow solution initially; a dark brown solid was isolated. Based on spectroscopic evidence such as IR, NMR, and UV of the product, they rationalized their observations as follows: At first, a charge-transfer complex **1** forms on mixing the reactants (a yellow solution). The  $\pi$  complex **1** then collapses to the dark-brown product **3** through an intermediate  $\sigma$  complex **2**. The intermediacy of **1** is important since succinic anhydride forms no complex or coloration with TEA. Spontaneous polymerization of MA in the presence of pyridine and trialkylamine has been reported.<sup>(76-78)</sup> Zwitterionic cyclic intermediates are proposed.



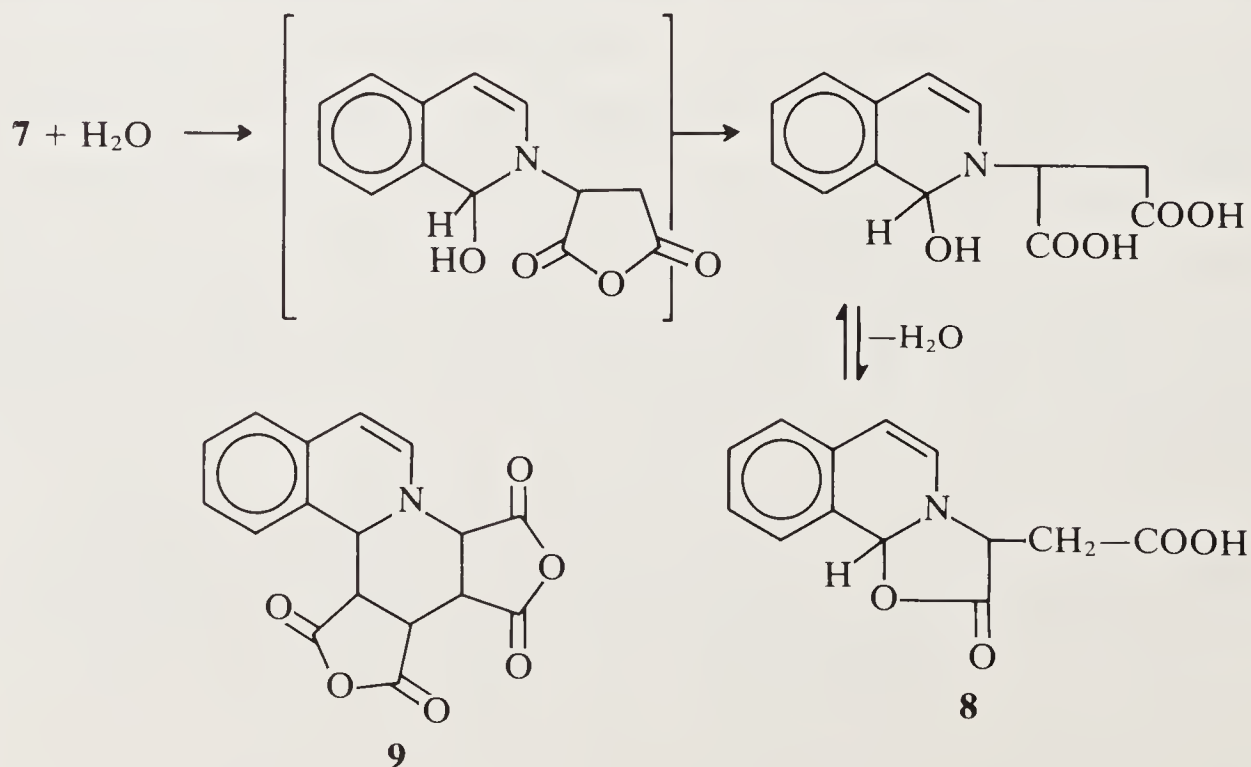
Maleic acid reacts with isoquinoline **4** in ether to form a betaine **5**.<sup>(3)</sup> Pyridinium maleate also gives excellent yield of the corresponding betaine. Trialkylamines gave no such adduct; only salts of fumaric acid were recovered.<sup>(90)</sup> No reasons for the differences are obvious but differences in amine basicity may be responsible.



The reaction of MA with isoquinoline **4** is solvent dependent and dependent on the concentration of MA. Rucinski *et al.*<sup>(4)</sup> observed that in ether solution MA formed the betaine **6** analogous to that from TEA. However,

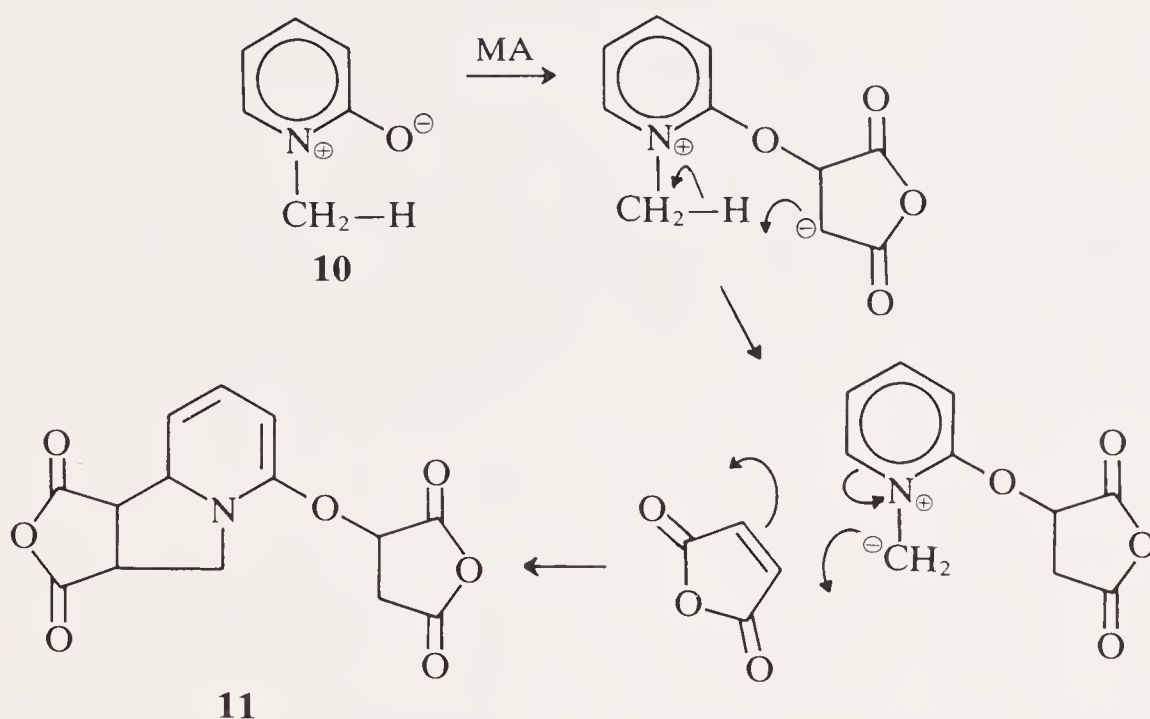


in benzene solution, ylid **7** was the main product. The ylid **7** has been isolated, identified, and derivatized. It reacts with water to yield a lactone **8**. The proposed scheme for the lactone formation is shown below: More interestingly,

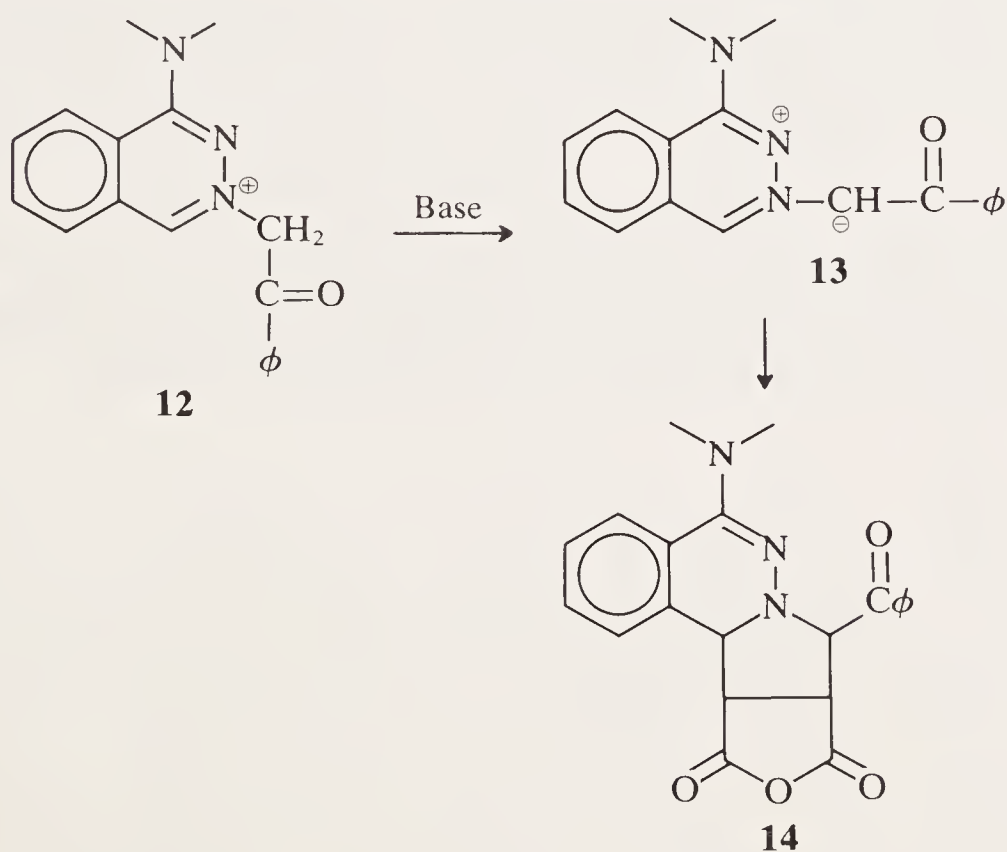


in the presence of another mole of MA, ylid **7** reacts further to give **9** which can also be obtained directly from MA and isoquinoline.

This reaction of MA with ylids has also been proposed by Thyagarajan and Rajagoplan in another case.<sup>(5)</sup> During an attempt to determine the aromaticity of *N*-alkyl-2-pyridines such as **10**, the condensation with MA was tried. The product that had two maleic acid residues was assigned the structure **11**. The following scheme was proposed for the formation of **11**, which decomposes on sublimation.

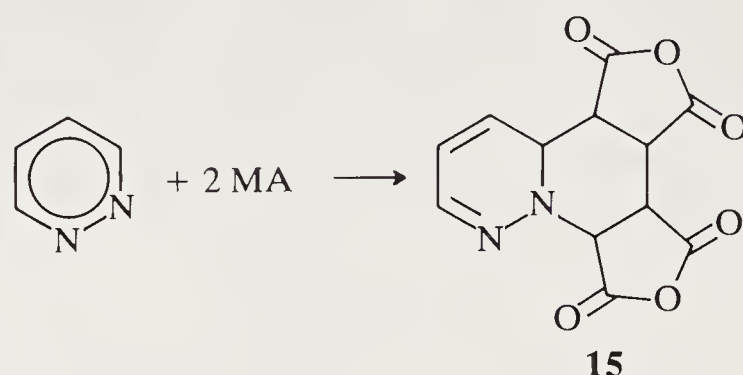


Similar ylid intermediates have been prepared in other cases and treated with MA to obtain analogous compounds. Guingant and Renault<sup>(11)</sup> have treated dimethylamine-1-phenacyl-3-phthalazininium bromide **12** with MA in the presence of triethylamine in chloroform. Ylid **13** was proposed to be formed which then added MA to give the product **14**.

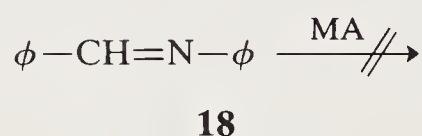
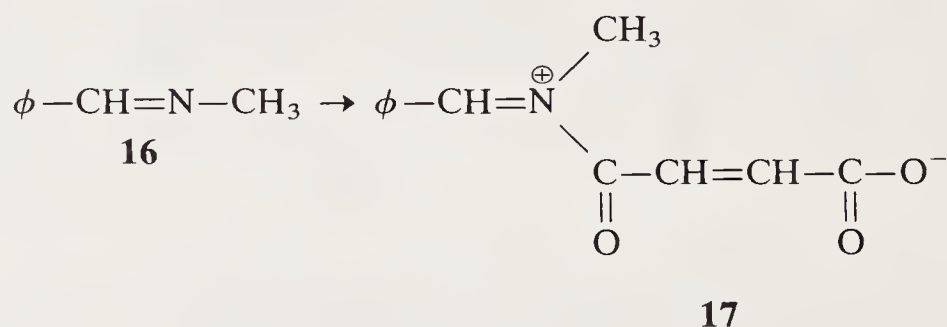




Cookson and Isaacs<sup>(6)</sup> have also observed a 2:1 MA:pyridazine adduct in an 85% yield. Based on an extensive spectroscopic analysis, they assigned structure **15** to the product.

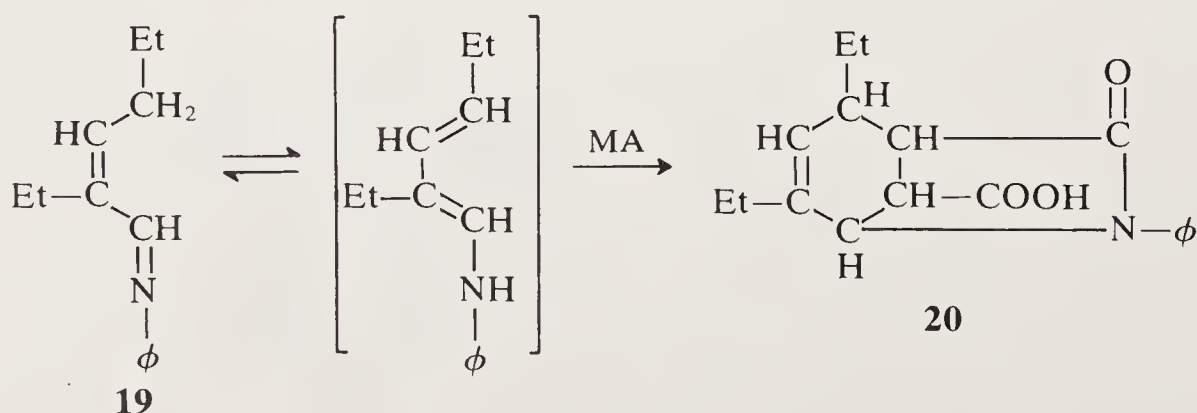


When the tertiary nitrogen reacting with MA is in the form of a Schiff's base, reaction varies depending on the nature of the Schiff's base. Van Alphen<sup>(1)</sup> isolated a yellow powder from a benzene solution of MA and benzaldehyde **16**. No yield was given but the structure **17** was proposed.

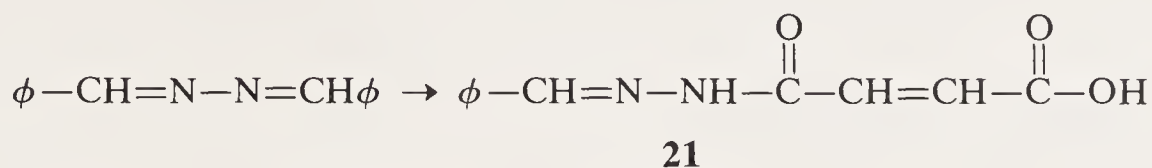


Benzalaniline **18**, however, gave no reaction if strictly anhydrous conditions were maintained.<sup>(7,8)</sup> Maleamic acid was isolated in some cases, probably resulting from the inadvertent inclusion of moisture.<sup>(7,9,10)</sup> This raises questions regarding structure **17** also. In a number of these reactions, the presence of moisture and its role may clarify the picture to some extent.

Schiff's base with  $\beta$ -unsaturation was examined by Snyder *et al.*<sup>(12)</sup> On treatment with MA, 2-ethyl-2-hexenylaniline **19** in benzene solution gave **20** as the product in a 75–80% yield. (See Chapter 4 for details.)

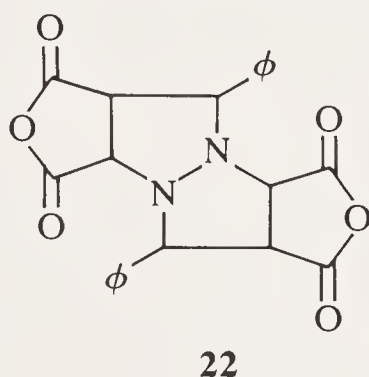


Azines were also examined by Snyder *et al.*<sup>(13)</sup> Benzaldehyde azine (benzalazine) with MA in ether saturated with water gave a maleamic acid derivative **21** in a 78% yield. Maleamic acid formation suggests that the rate of azine hydrolysis may be faster than that of MA under these conditions.



Similar results have been obtained with ketazines by Caronna.<sup>(7,14)</sup> Although not indicated, moisture was necessary to explain the product.

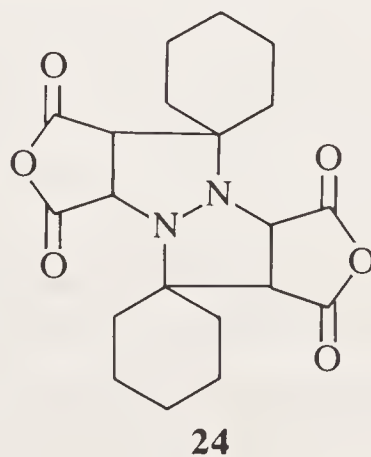
Wagner-Jauregg<sup>(15)</sup> obtained a small amount of a product on refluxing benzaldehyde azine with MA in benzene solution. Since the product contained 2 moles of MA per mole of the azine, he assigned it structure **22**.<sup>(16)</sup>



Van Alphen<sup>(17)</sup> claimed higher yields for this product (yield not reported). The structure and hence the criss-cross addition of the 1,3-dipolar type was confirmed.<sup>(18,19)</sup>

It is also interesting to note that acetaldazine gave a different product which was not identified. Van Alphen<sup>(17)</sup> also reported a coproduct that was soluble in alcohol unlike **22**, but no information was given on that product. Furthermore, when benzalazine was reacted with only 1 mole of MA, a yellow resin was obtained which on further treatment with MA did not give **22**.

Dutt and Guha<sup>(20)</sup> have examined cyclohexanone azine **23** and observed that the nature of the product is dependent on the reaction conditions. In ether, **23** and MA gave the maleamic acid derivative similar to that obtained by Caronna.<sup>(7,14)</sup> On the other hand, in aromatic solvents the criss-cross adduct



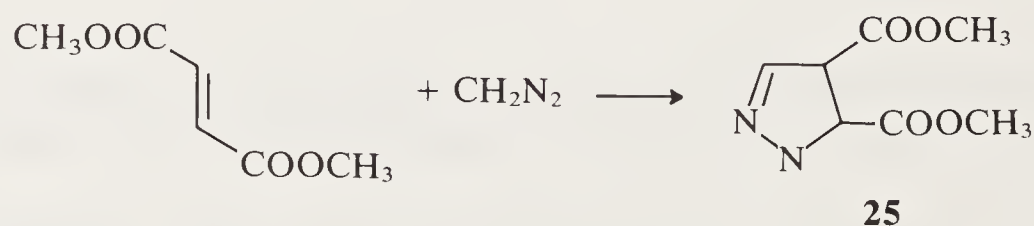
**24** was formed in low yield on allowing the reaction between 2 MA : 1 **23**. This may merely reflect that ether is more hygroscopic than the aromatic solvents. Thus, influence of the reaction conditions is not truly demonstrated by Dutt and Guha.<sup>(20)</sup>

### 7.3. 1,3-DIPOLAR REAGENTS

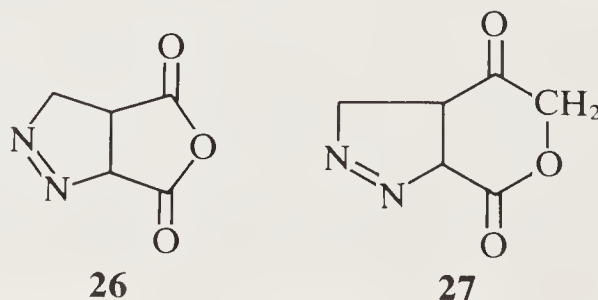
Above we saw a criss-cross addition of benzalazine with MA involving two 1,3-dipoles. A number of other reagents which fall in the class of 1,3-dipoles, e.g., diazoalkanes, nitrile oxides, and azides, also react with MA to yield intermediates with unique structural features. Many of these products are formed in good yields, thus increasing their importance as intermediates for the synthesis of other compounds, such as pharmaceuticals and monomers.

#### 7.3.1. Diazo Compounds

The reaction of diazomethane with dimethyl fumarate was reported by Von Pechmann to give the diester of 2-pyrazoline-4,5-dicarboxylic acid **25**.<sup>(21,26)</sup> The product was isolated as the acid after hydrolysis.



Hampel<sup>(21)</sup> has examined the reaction of MA with diazomethane. The reaction in ether at 5°C gave an 85% yield of the product expected by the 1,3-dipolar cycloaddition to MA and was assigned structure **26**. No comment

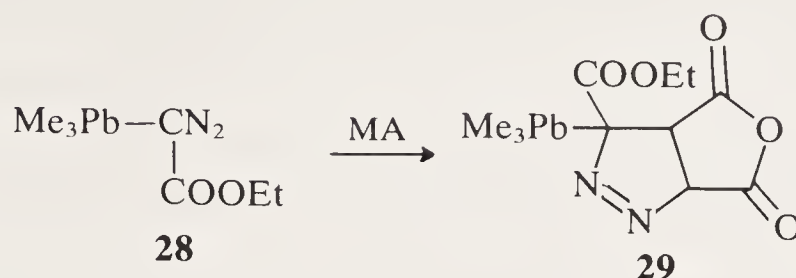


was made about the different olefin assignments in **25** and **26**. Hampel assigned the IR absorption at  $1680\text{ cm}^{-1}$  to the  $-\text{N}=\text{N}-$  bond. In view of the easy reactivity of MA with secondary amines such as **25**, the structural assignment as in **26** appears correct. Reaction at 20°C gave a further ring-expanded lactone **27** in a 72% yield when the two reactants were added simultaneously.

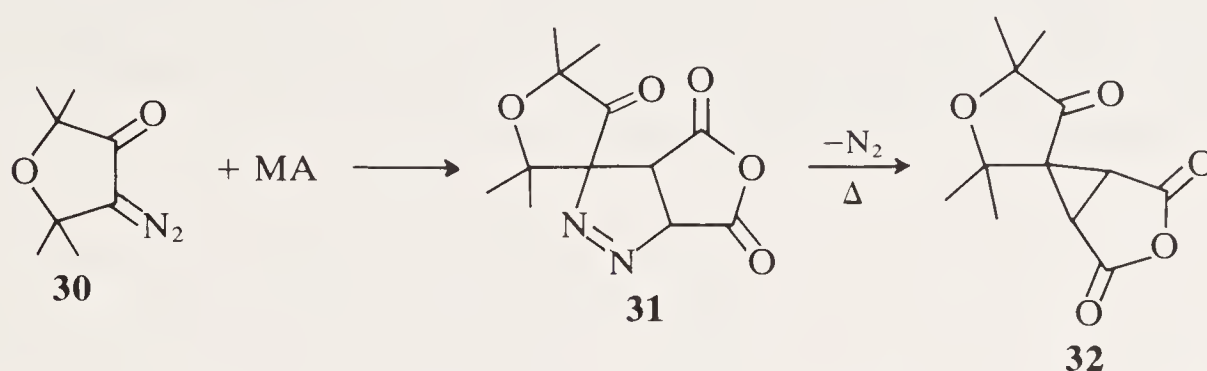
Substituted diazoalkanes could react similarly. Gruning and Lorberth<sup>(22)</sup> have studied the addition reaction of trimethyllead diazoacetic ester **28** with MA to obtain an 85% yield of the pyrazoline derivative **29**. Maleic acid and



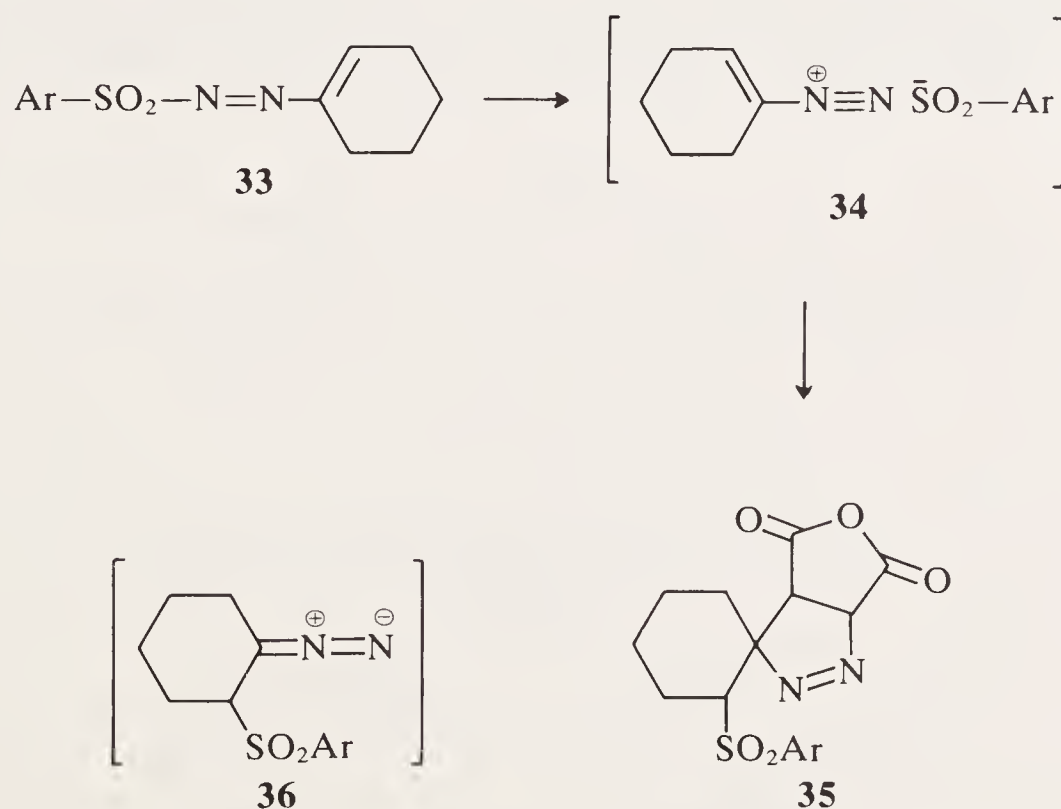
dimethyl maleate also reacted to give the respective derivatives in 60% and 52% yields.



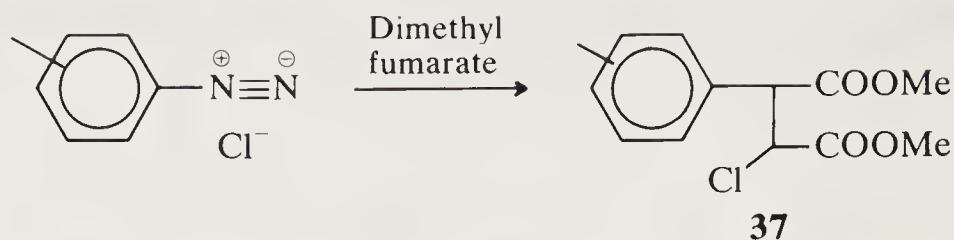
A variety of substituted diazoalkanes have been examined. Rodina *et al.*<sup>(23)</sup> reported formation of a spiro pyrazoline **31** from the cyclic diazoketone **30**. The product on further heating to 141°C loses 1 mole of N<sub>2</sub> to yield a spiro cyclopropane derivative **32**.



DeMaria *et al.*<sup>(24)</sup> examined the reaction of 1-(*p*-tolylsulfonyl)-azocyclohexene **33** with MA and its derivatives. The reaction, which proceeds through formation of the proposed intermediate cyclohexene-diazonium salt



**34**, gave **35** as the product. However, this behavior is reminiscent of diazoalkanes, so intermediacy of the diazoalkane **36** cannot be ruled out. Furthermore, note that diazonium salts such as aryldiazonium chloride react with dimethyl fumarate to give an addition product **37**.<sup>(25,26)</sup> Based on their

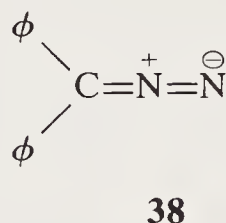


investigation, DeMaria assigned the following order of reactivities for various MA derivatives:



It may be noted that the overall reactivity differences were small, although MA was the most reactive.

Huisgen *et al.*<sup>(27)</sup> have studied the relative reactivity of diphenyldiazomethane **38** with MA and other olefins. Their results are summarized in Table 7.1. The observed reactivity order was obtained at 40°C in DMF. MA was the most reactive polarophile examined.



### 7.3.2. Azides

Benzyl azide **39** ( $\text{R} = \text{Ph}-\text{CH}_2-$ ) reacts with dimethyl fumarate to form a triazoline derivative **40**.<sup>(28)</sup> Similarly, carbamyl azide **39** ( $\text{R} = \text{NH}_2-\text{CO}-$ )

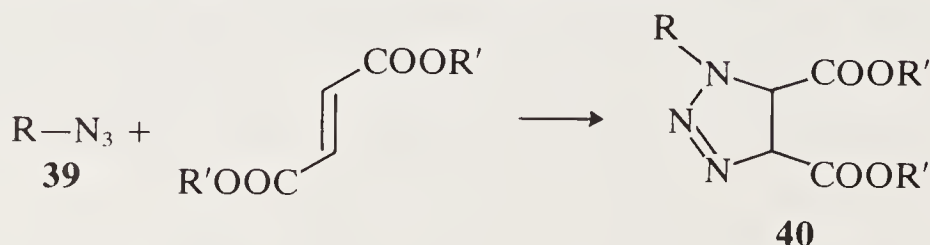


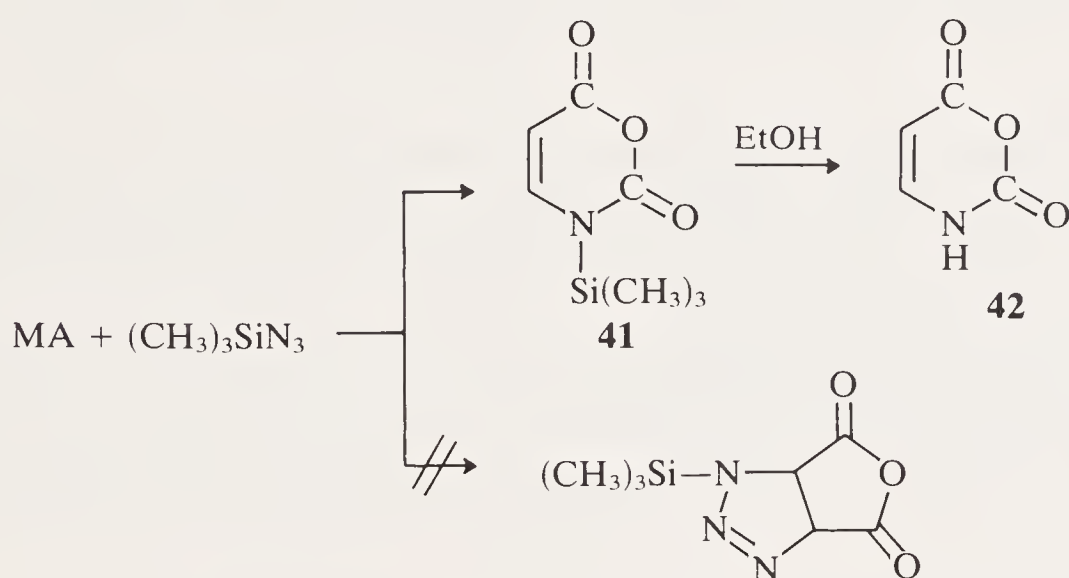
Table 7.1. Relative Reactivity of **38** with Olefins<sup>a</sup>

Olefin	Relative rate
Styrene	1.0
Ethyl crotonate	1.75
Dimethyl maleate	48.9
Dimethyl fumarate	1 750.0
MA	4 164.0

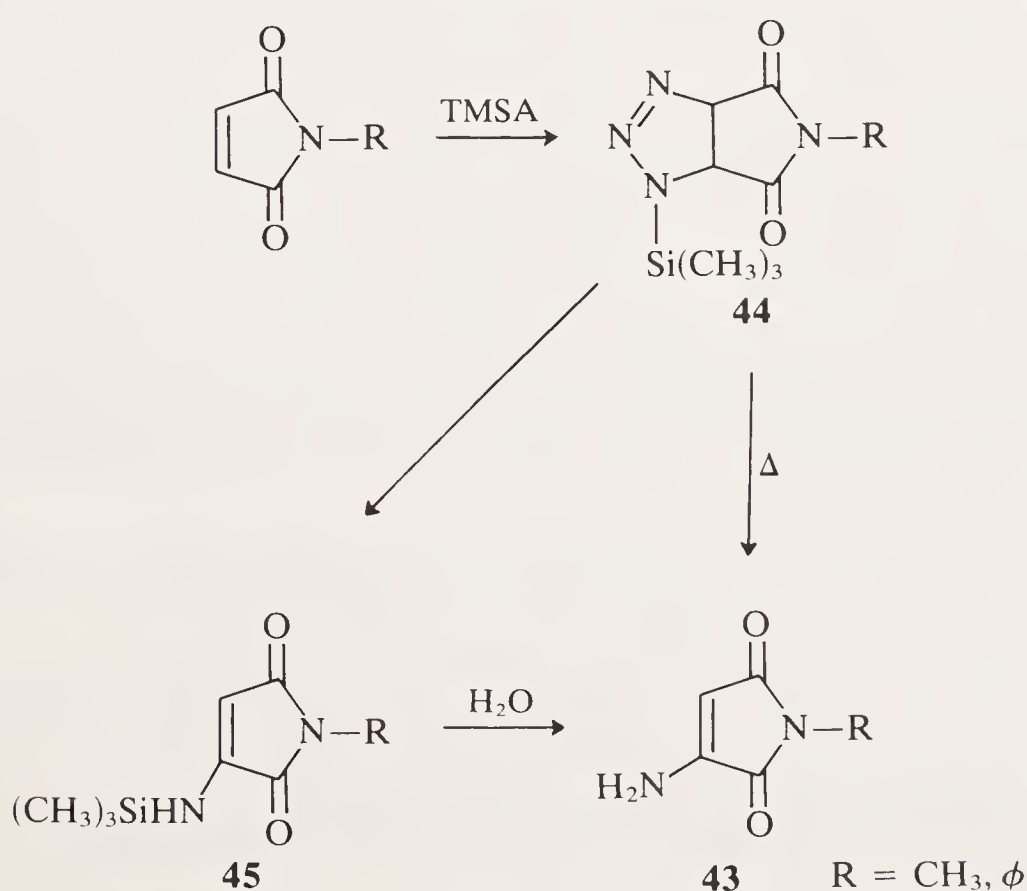
<sup>a</sup> From Reference 27.

was also reacted with diethyl fumarate.<sup>(29)</sup> Dialkyl maleate gave a much poorer yield. Huisgen *et al.*<sup>(30)</sup> have examined the kinetics of the reaction of aryl azides with MA, *N*-phenylmaleimide, etc.<sup>(30)</sup>

Earlier, we observed that diazomethane reacts with MA at 20°C to yield a ring-enlarged lactone **27** due to carbene insertion into the OC—O bond of the anhydride. It has been observed that trimethylsilyl azide (TMSA) instead inserts into the bond between the olefinic carbon and carbonyl grouping. No triazoline derivative was reported. Washburne *et al.*<sup>(38)</sup> utilized this reaction to synthesize oxauracils. They treated MA with TMSA to obtain the silyl derivative **41** which could be converted to oxauracil **42** in a 60–80% overall

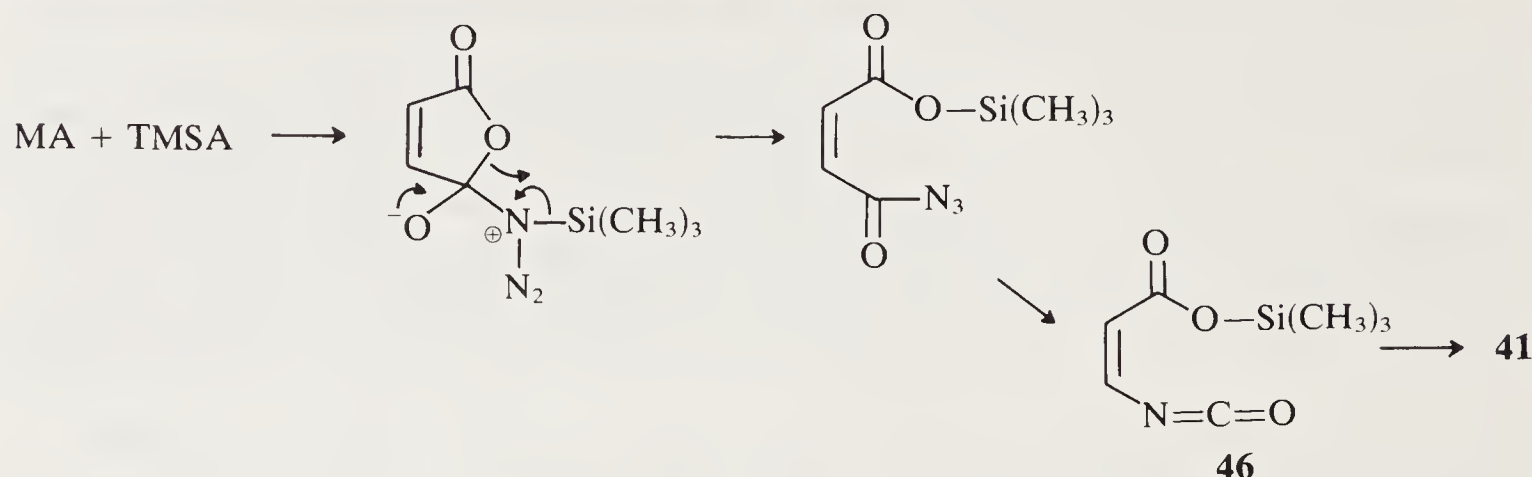


yield.<sup>(38,39)</sup> *N*-methylmaleimide, on the other hand, gave aminomaleimide derivative **43**, which results from a 1,3-dipolar cycloaddition to give **44**, followed by loss of N<sub>2</sub>, as shown below. *N*-phenylmaleimide behaves similarly.



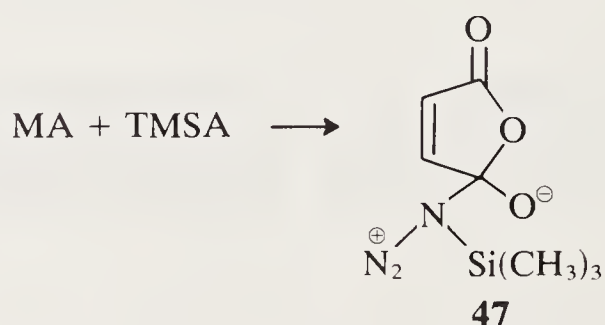


Based on a detailed study of the TMSA reaction with MA, Washburne *et al.*<sup>(38)</sup> proposed the following scheme involving an isocyanate **46** intermediate for the formation of oxauracil **41**.\*



It was concluded from NMR studies of the reaction of TMSA with MA and other anhydrides that isocyanates like **46** may exist in equilibrium with *N*-carboxyanhydrides like **41**. The position of this equilibrium for various anhydrides is shown in Table 7.2.

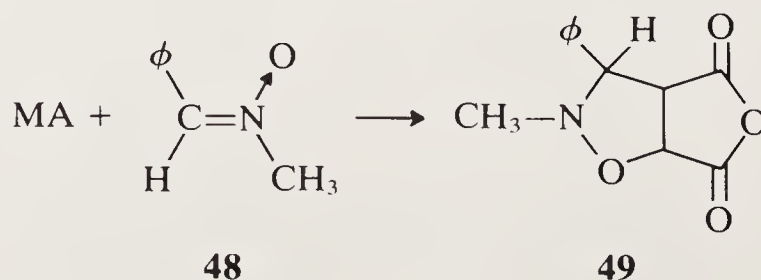
The simpler mechanism shown below was ruled out on the basis that intermediate **47** is similar to the one produced from the reaction of aldehydes with TMSA, which requires Lewis acid catalysis for rearrangement whereas the reaction in question needs no catalyst.



The oxauracil formation has also been applied to substituted maleic anhydrides.<sup>(40)</sup>

### 7.3.3. Nitrones

Huisgen *et al.*<sup>(31)</sup> studied the reaction of *N*-methyl-C-phenylnitrone **48** with MA and its derivatives. With MA as a reactant, in toluene, a very high



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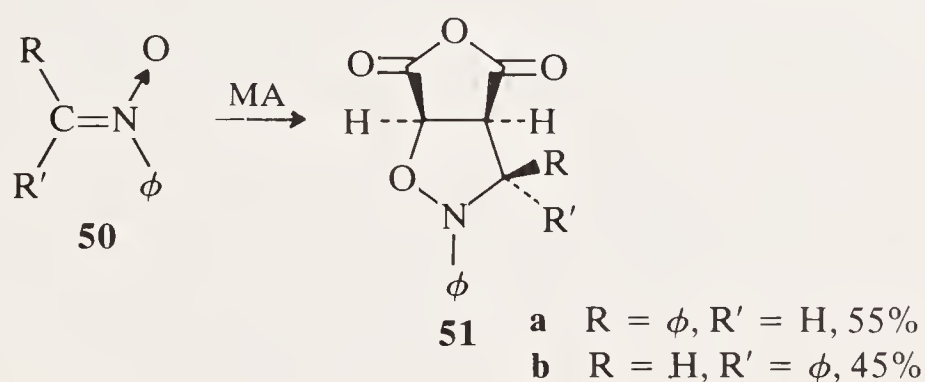
Table 7.2. Position of the *N*-Carboxyanhydride-Isocyanate Equilibrium<sup>a</sup>

Anhydride	% Product	
	<i>N</i> -Carboxyanhydride	Isocyanate
Succinic	0	100
Hexahydrophthalic	20	80
Phthalic	20	80
Maleic	100	0

<sup>a</sup> Reprinted with permission from *J. Org. Chem.* **37**, 1738 (1972). Copyright © 1972, American Chemical Society.

yield of the isoxazoline adduct **49** was obtained. Similarly, 3,4-di-hydro-isoquinoline oxide was also employed as a reagent.

Joucla and Hamlein<sup>(32)</sup> treated MA with C-phenyl-*N*-phenylnitrone **50** in refluxing benzene and obtained two stereoisomers of isoxazolidine **51a** and **51b** in quantitative yield. However, the C-benzoyl-*N*-phenylnitrone gave only **51b** ( $R' = \phi\text{CO}$ ). When the esters of maleic or fumaric acid were utilized, various proportions of stereoisomers were obtained.



Huisgen *et al.*<sup>(33)</sup> have studied the kinetics of the reaction of **48** with a variety of olefins. Table 7.3 gives some selected data of the relative reactivities in toluene solution. Of all the olefins examined, MA was the most reactive. Recently, Russian workers have studied the kinetics of the reaction of MA with nitrones.<sup>(101)</sup> Activity of the nitrone was reported to parallel the exothermicity of the reaction.

#### 7.3.4. Nitrile Oxides, Imines, and Sulfides

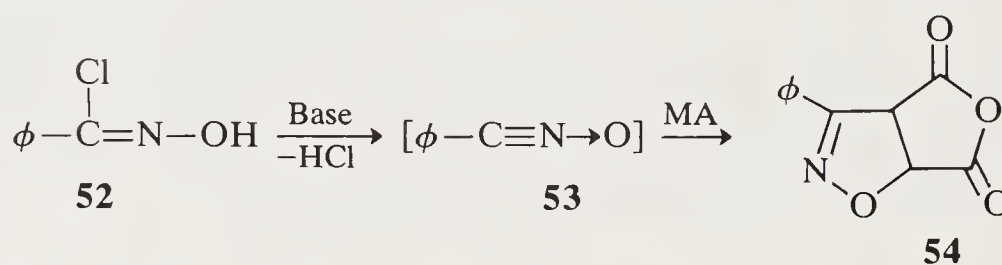
The isoxazole nucleus that could be synthesized from nitrones can also be obtained from 1,3-dipolar cycloaddition of nitrile oxides. Quilico *et al.*<sup>(34)</sup> generated benzonitrile oxides **53** from the benzhydroxamic acid chloride **52** precursor. The reaction involving MA with **52** gave, on work-up, a 77% yield of the adduct **54**.

Table 7.3. Relative Rates of the Reaction of **48** with Various Olefins in Toluene Solution<sup>a</sup>

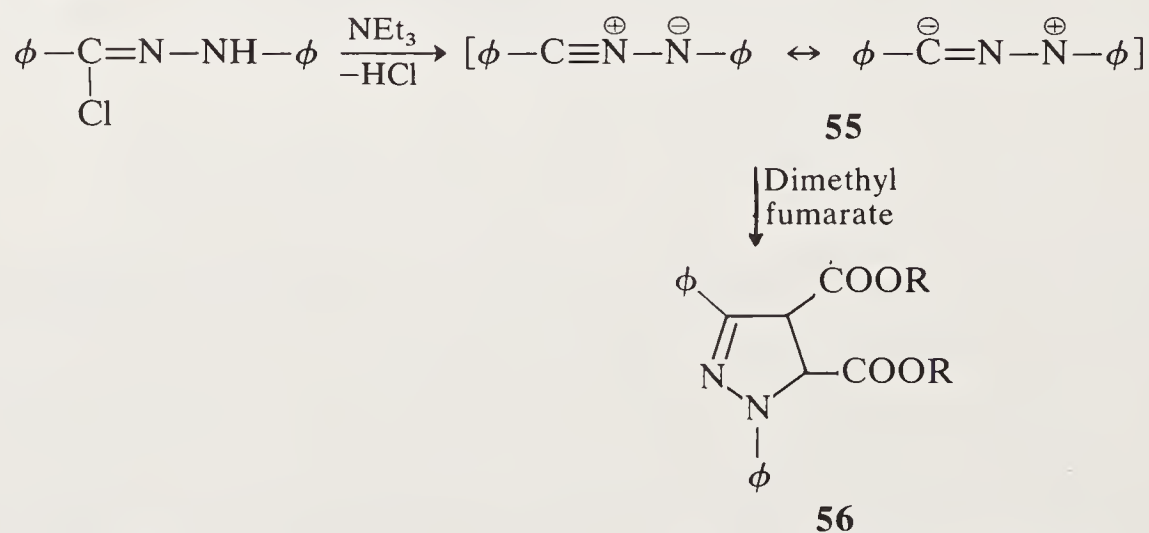
Olefin	Relative reactivity	
	85°C	120°C
Methyl acrylate	1	1 <sup>b</sup>
Acrylonitrile	0.7	0.7 <sup>b</sup>
Styrene	—	0.03
Heptene-1	—	0.006
MA	22.9	17.3 <sup>b</sup>
Fumaronitrile	3.8	3.3 <sup>b</sup>
Diethyl fumarate	1.6	1.6 <sup>b</sup>
Diethyl maleate	0.6	0.6 <sup>b</sup>

<sup>a</sup> From Reference 33.

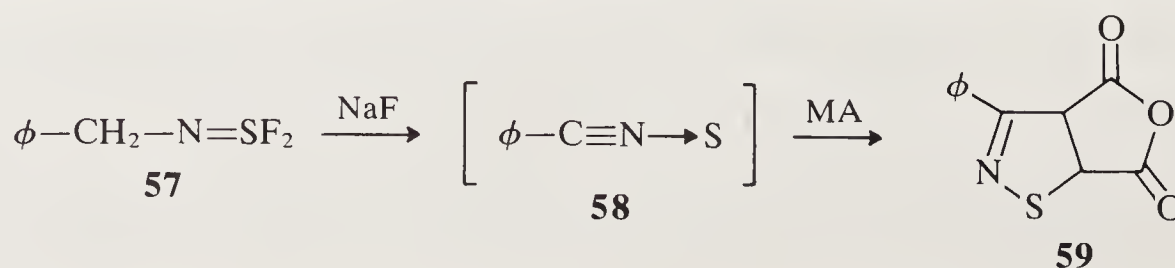
<sup>b</sup> Extrapolated.



Nitrile imines **55** add to dimethyl fumarate to yield 99% of the pyrazoline derivative **56**.<sup>(35)</sup>

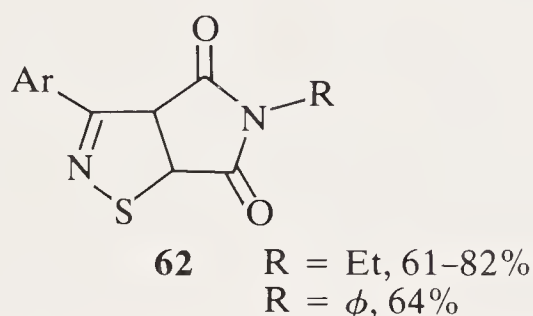
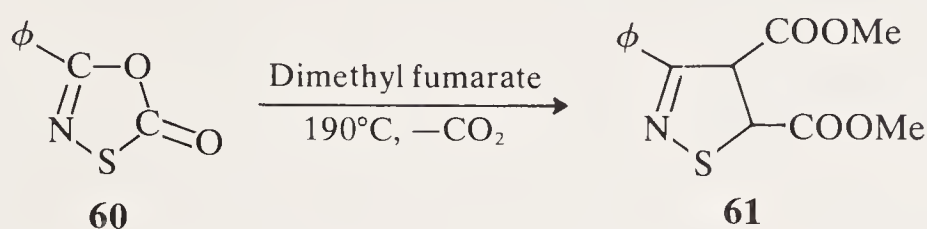


Nitrile sulfides **58** also can be generated *in situ*. Gunwell and Dye<sup>(36)</sup> obtained a 20% yield of 3-phenyl-2-isothiazoline-*cis*-4,5-dicarboxylic anhydride **59** by the treatment of **57** with MA in the presence of sodium fluoride:



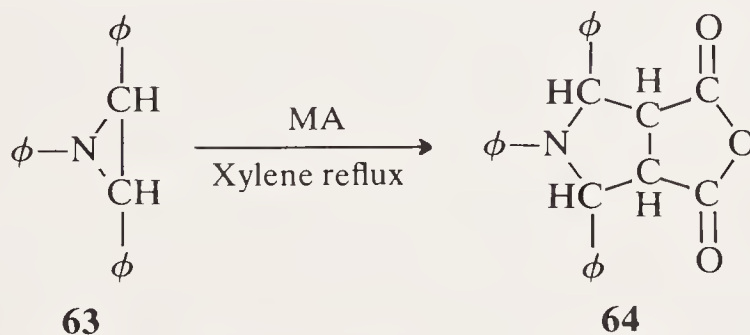


Howe and Franz<sup>(37)</sup> have recently obtained nitrile sulfide intermediates via thermolysis of 5-substituted 1,3,4-oxathiazol-2-one **60**. Thermolysis of the latter in the presence of an excess of dimethyl fumarate at 190°C gave **61** in a 45–55% yield. Similarly, *N*-alkyl and *N*-arylmaleimides gave good yields of the heterocycles **62**.

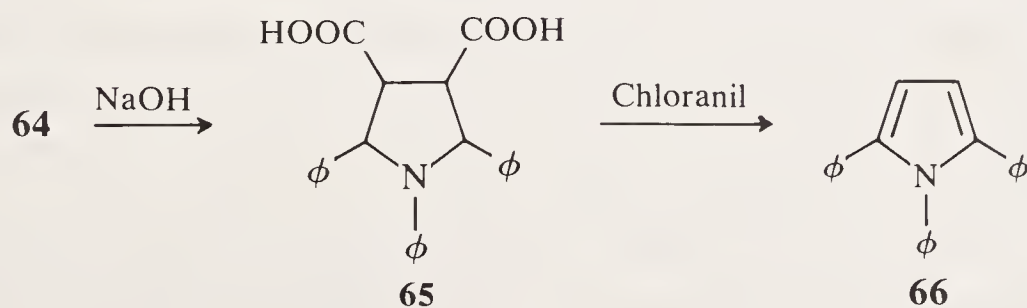


### 7.3.5. Aziridines

Heine and Peary<sup>(41)</sup> have reported a reaction of 1,2,3-triphenylaziridine **63** with MA involving scission of a C–C bond of the aziridine ring. Thus, refluxing **63** and MA in *p*-xylene solution gave a 94% yield of 1,2,5-triphenylpyrrolidine-3,4-dicarboxylic anhydride **64**.



The proof of structure was obtained by the hydrolysis of **64** to the diacid **65** followed by simultaneous oxidation and decarboxylation of the latter with chloranil to 1,2,5-triphenylpyrrole **66**.



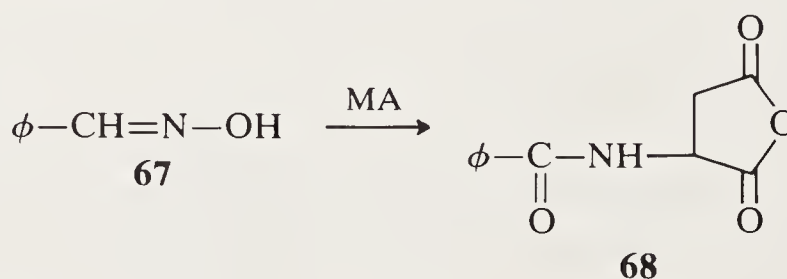
It may be noted that C–C bond cleavage of tetracyanoethylene oxide during the addition to olefin has been reported.<sup>(42)</sup> This reaction can be

rationalized in terms of a 1,3-dipolar intermediate generated from the oxide. As seen in Chapter 6, photochemical addition of stilbene oxides to MA also gives a product reminiscent of 1,3-dipolar addition.<sup>(89)</sup> This may further suggest the possibility of a singlet intermediate in the photochemical process. The scope of such reactions of MA would be interesting to examine.

## 7.4. OTHER REAGENTS

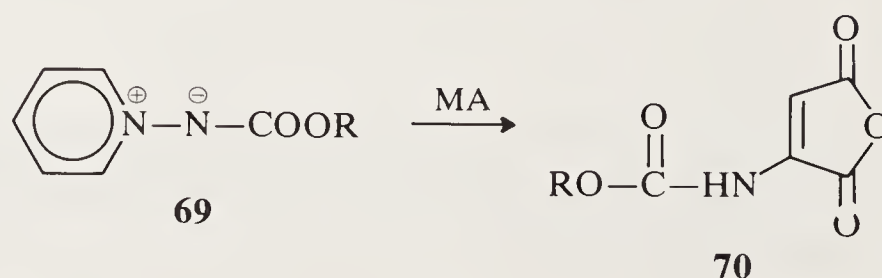
### 7.4.1. Oximes

LaParolla<sup>(43,44)</sup> found that benzaloxime **67** on heating with MA yields an aspartic acid derivative **68** as a product. Obviously, the reaction involves a Beckmann rearrangement during the transformation. Anhydrides are known to be good reagents for that purpose. The overall mechanism is probably not simple and deserves attention from the product as well as chemistry aspects.

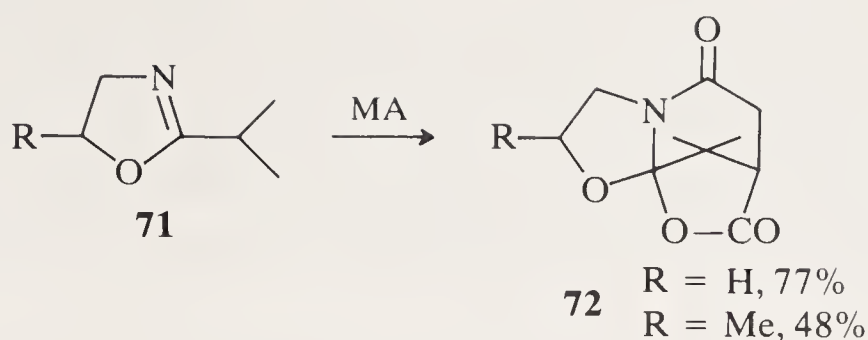


### 7.4.2. Aminimides

Aminimides also enter into a reaction with MA derivatives. *N*-ethoxycarbonyliminopyridinium ylide **69** gives a 73% yield of the adduct **70**. *N*-phenylmaleimide is also reported to yield an analogous product.<sup>(45)</sup> Dialkyl fumarate and maleate also undergo similar reaction.

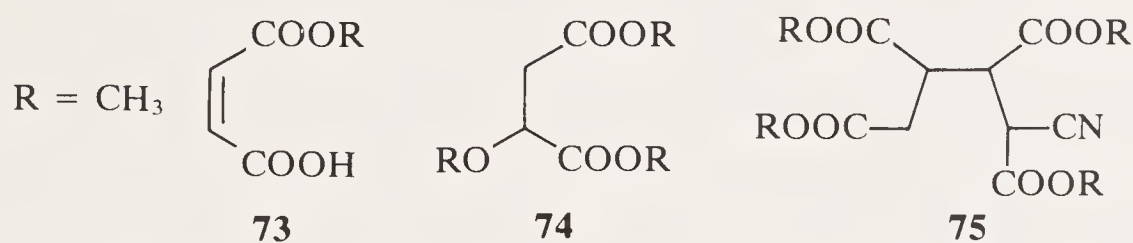


A very unusual reaction of 2-isopropyl-2-oxazoline **71** ( $\text{R}=\text{H}$ ) needs mention. Nehring and Seelinger<sup>(88)</sup> reported that on refluxing a 1,2-dichloroethane solution of **71** and MA, a 77% yield of the product **72** was obtained. When  $\text{R} = \text{methyl}$ , a 48% yield of a similar adduct was formed. The structure was proved by NMR, IR spectroscopy, elemental analysis, and hydrolysis studies. It is interesting to note that the hydrogen atom of the isopropyl group is so active for Michael addition, since that would be required as part of the sequence.

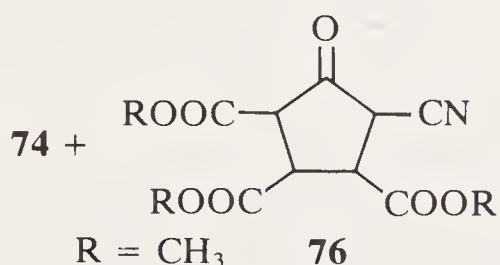


### 7.4.3. Hydrogen Cyanide

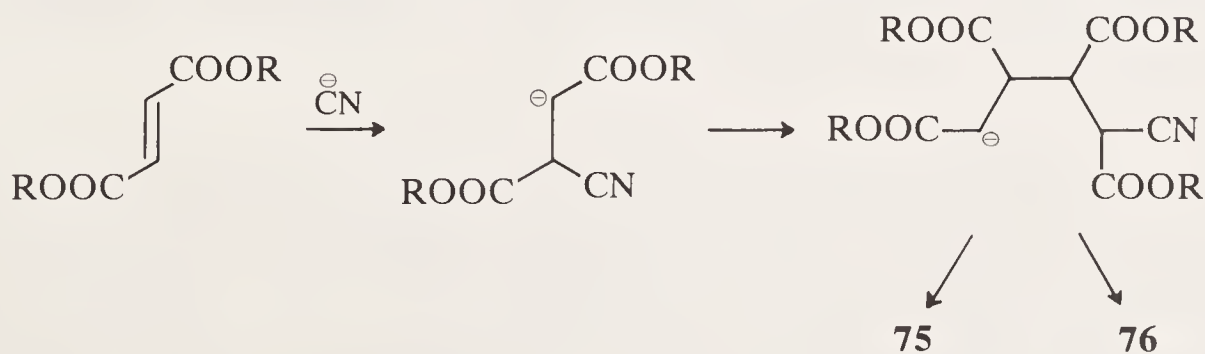
This reaction, although it involves esters of MA, appears synthetically very useful. Dialkyl esters of MA react with HCN to yield different products depending on the reaction conditions. Michael and Weiner<sup>(46)</sup> observed that on allowing a 10% aqueous methanol solution of dimethyl fumarate and KCN to react at room temperature, three products were obtained: **73**, **74**, and **75**.



In anhydrous methanol, on the other hand, two main products obtained were **74** and a cyclopentanone derivative **76** after 6 days at room temperature.



The crude yield of **76** could be increased to 75% by refluxing the mixture for 2 h. Obviously, the reaction is initiated by a nucleophilic attack by  $\text{CN}^-$  on the fumarate, leading to the products **75** and **76** according to the scheme below.

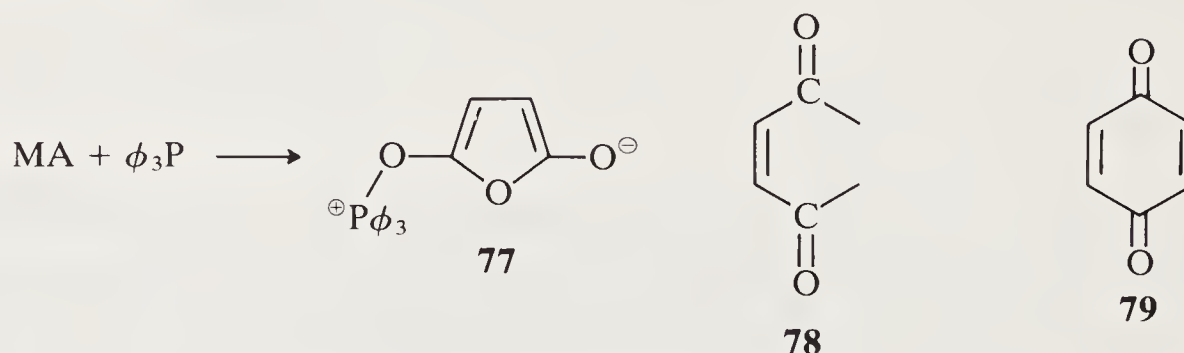


### 7.4.4. Phosphorus Compounds

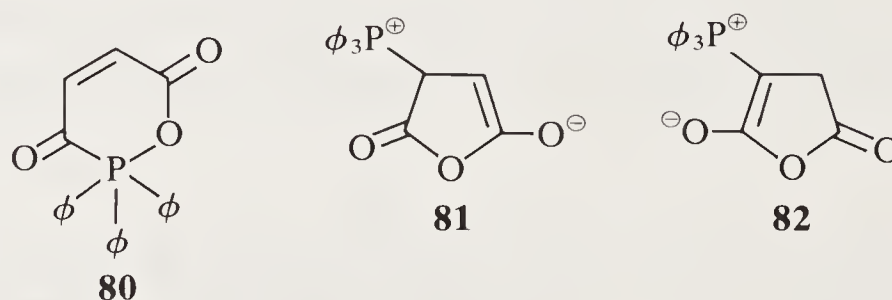
Schonberg and Ismail<sup>(47,48)</sup> observed that a permanent orange-red color is produced when a trace of MA is added to a colorless solution of



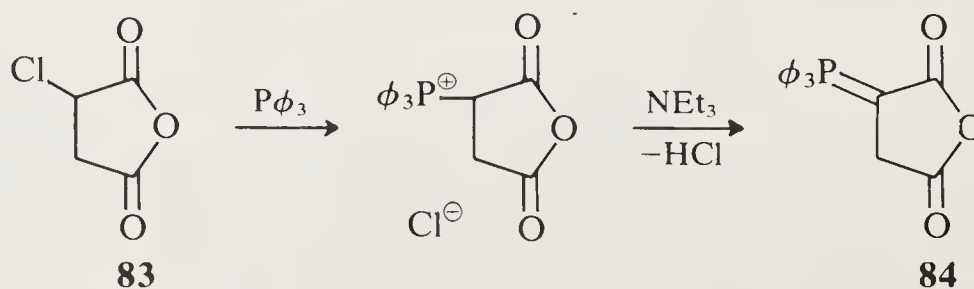
triphenylphosphine in chloroform or benzene. They incorrectly proposed structure **77** for the adduct and suggested that structural grouping **78** was necessary for crystalline adduct formation from MA and triphenylphosphine. The latter conclusion was based on the observation that benzoquinone **79** gave a similar adduct but succinic anhydride did not.<sup>(47)</sup> Anthraquinone also failed to give the adduct.



During the late 1950s and early 1960s interest was regenerated into the outcome of the reaction and a number of groups studied this reaction. Ramirez *et al.*<sup>(49)</sup> proposed structure **80** since a five coordinated phosphorus compound was isolated. Structure **81** was proposed by Horner and Klupfel<sup>(50)</sup> based on conjugate addition, whereas Aksnes<sup>(51)</sup> proposed structure **82** based on infrared spectroscopic study.

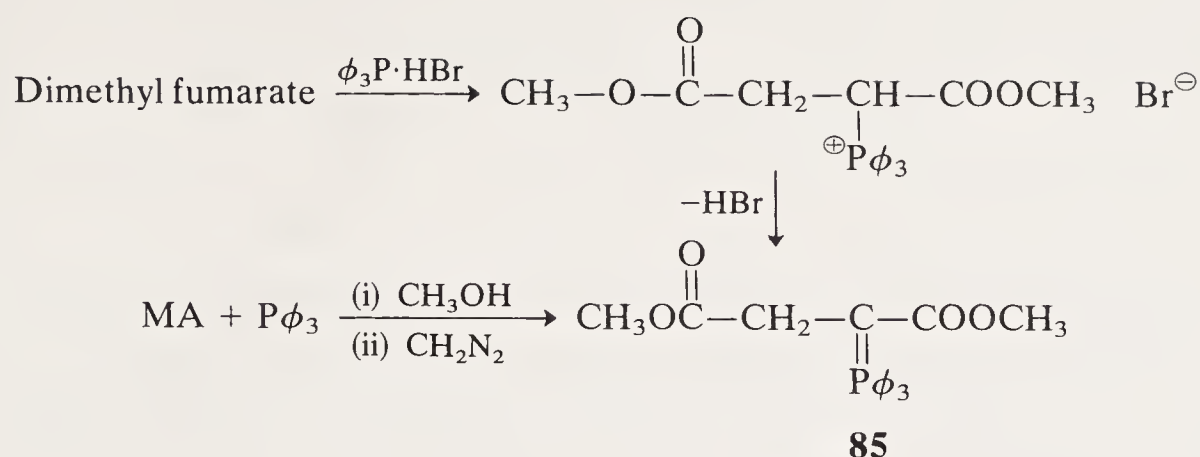


Chopard and Hudson<sup>(52)</sup> studied the NMR spectrum of the adduct and observed two methylenic hydrogen atoms, thus ruling out structures **77**, **80**, and **81**. Hudson and Chopard<sup>(53)</sup> also examined the reaction of chlorosuccinic anhydride **83** with triphenylphosphine in THF, followed by treatment with triethylamine, and obtained a betaine **84**. (This product is identical to that obtained from direct reaction of MA +  $\text{P}\phi_3$ .)

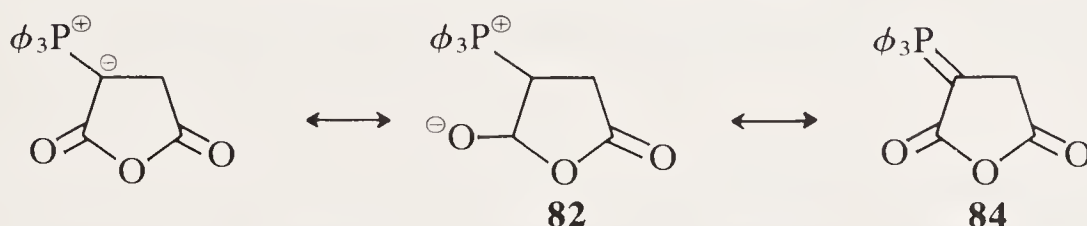


Osuch *et al.*<sup>(54)</sup> observed that the product obtained from treatment of the triphenylphosphine:MA adduct with methanol followed by esterification with diazomethane and that obtained from the following reactions of dimethyl

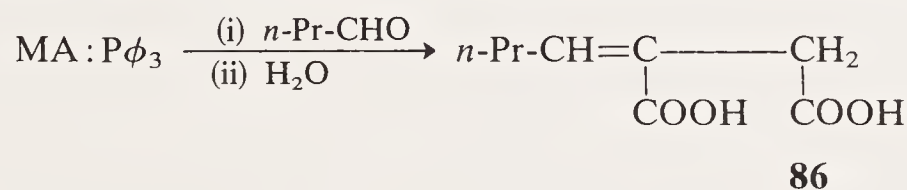
fumarate were identical **85**:



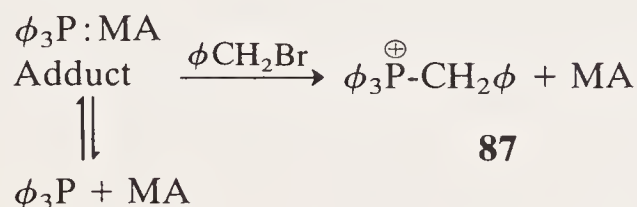
Thus, the evidences of Hudson and Chopard<sup>(52,53)</sup> and Osuch *et al.*<sup>(54)</sup> lead to the conclusion that the adduct is a phosphobetaine and the true structure could be represented by a resonance system.



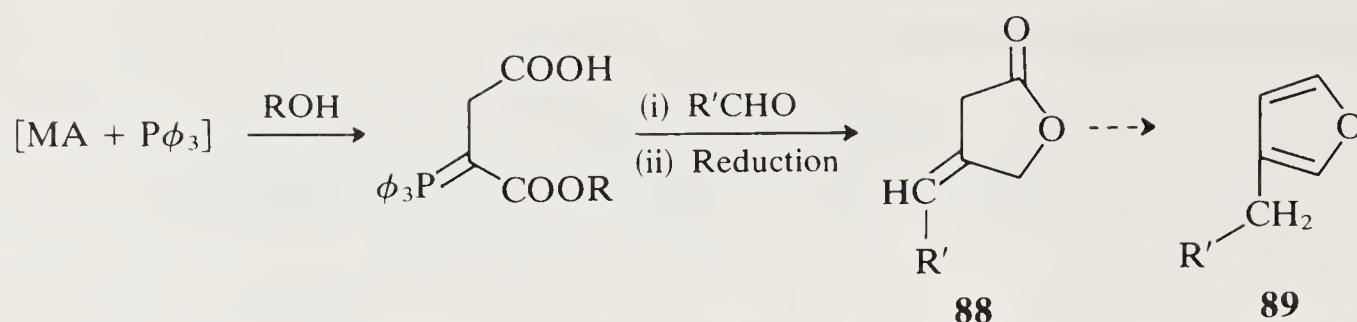
The phosphorane adduct reacts with *n*-butyraldehyde as expected, although low yields of *n*-propylitaconic acid **86** are obtained.



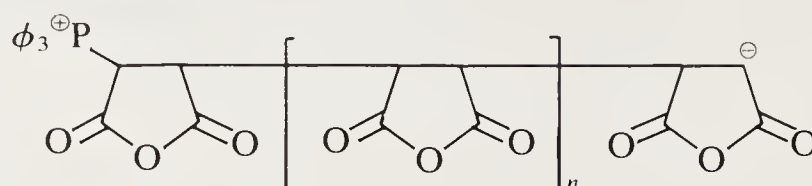
Interestingly, however, the reaction with benzyl bromide yields benzyltriphenylphosphonium bromide **87** and MA. This suggests<sup>(53)</sup> that the adduct formation is reversible and that, in solution, a significant quantity of MA and  $\text{P}\phi_3$  may be present.



McCurry and Donovan<sup>(59)</sup> have employed the ylid adduct for the synthesis of alkylidene lactone **88** in high yields (60–78%). The latter are precursors to 3-alkylfurans **89**. Use of the ylid **84** has been reported in the synthesis of lysergic acid<sup>(60)</sup> and as a catalyst for the preparation of phosphine sulfides.<sup>(61)</sup> Zweifel and coworkers<sup>(78–80)</sup> have studied the triphenylphosphine and tributylphosphine initiated polymerization of MA. A zwitterionic system is claimed to be responsible for this anionic polymerization<sup>(79,80)</sup> since the product contained succinic anhydride units along with triphenylphosphine.

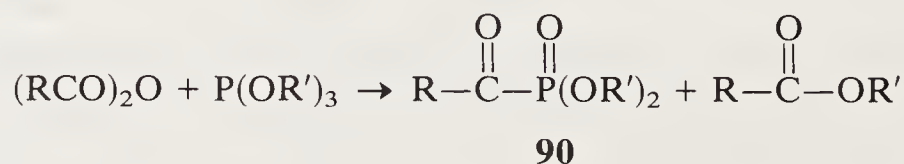


However, the structure of the polymer has other units such as a cyclopentanone moiety, formed by rearrangement. The use of tributylphosphine involves a loss of  $\text{CO}_2$  and is slightly more complex (see Chapter 8). Furthermore, cyclic anhydrides do react with ylids.<sup>(100,103)</sup> Contribution of such reaction in the polymerization is not clear at present.

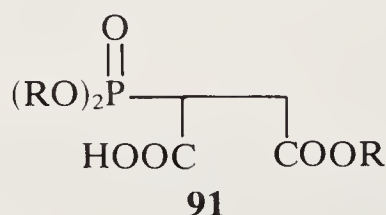


Reaction of these phosphorus compounds and of those covered earlier lead to intermediates of interest such as monomers, insecticides, fungicides, and pharmaceutical products. Their chemistry and potential is far from being fully exploited.

Not much is known about the reaction of trialkyl phosphites with MA. For example, it is known that acid anhydrides will react with trialkyl phosphites to give phosphinic acid derivatives **90** via Arbuzov rearrangement as depicted below.<sup>(55)</sup> However, Kamai and Kukhtin<sup>(56)</sup> observed a very exothermic reaction between MA and trialkyl phosphite. No characterizable product could

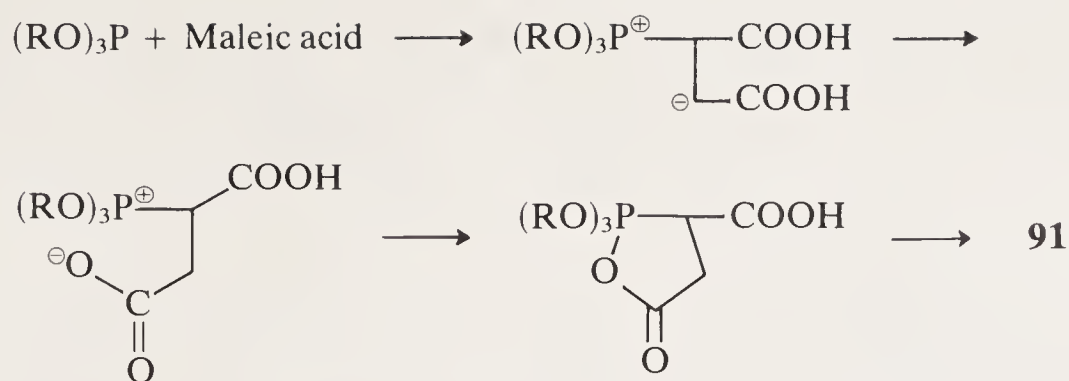


be obtained from the resinous reaction mass. Maleic acid, on the other hand, reacts with trialkyl phosphite to give a low yield of adduct **91**.<sup>(57,58)</sup> The



reaction is very exothermic and cooling is necessary. If cooling is not provided, a violent evolution of  $\text{CO}_2$  takes place giving a decomposed mass. In this event, one wonders if the yields could be significantly improved by adding maleic acid to the phosphite. For the production of **91**, Kamai *et al.*<sup>(57)</sup> proposed the following scheme:

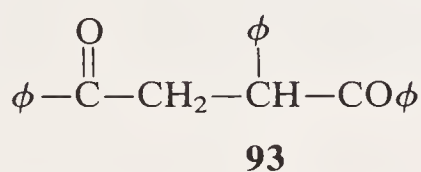
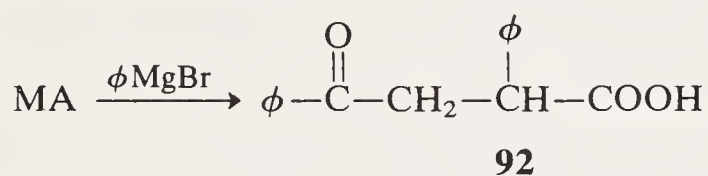




#### 7.4.5. Organometallic Compounds

The earliest investigations of these types of reactions centered on Grignard reagents<sup>(62,63)</sup> and hexaphenyldilead.<sup>(64)</sup> As expected, the multiplicity of reactive centers on MA does pose a formidable problem for having a selective reaction.

Tarbel<sup>(62)</sup> examined the reaction of phenylmagnesium bromide with MA. Among the products were **92** and **93**.



Weizmann and Bergmann<sup>(63)</sup> treated MA with an excess of benzyl, ethyl, and butyl Grignards. In each case, a mixture of acidic and neutral products was obtained. The acidic fraction contained  $\gamma$ ,  $\gamma$ -dialkyl- $\gamma$ -hydroxycrotonic acid **94**. The latter cyclized spontaneously to give **95** but could be trapped

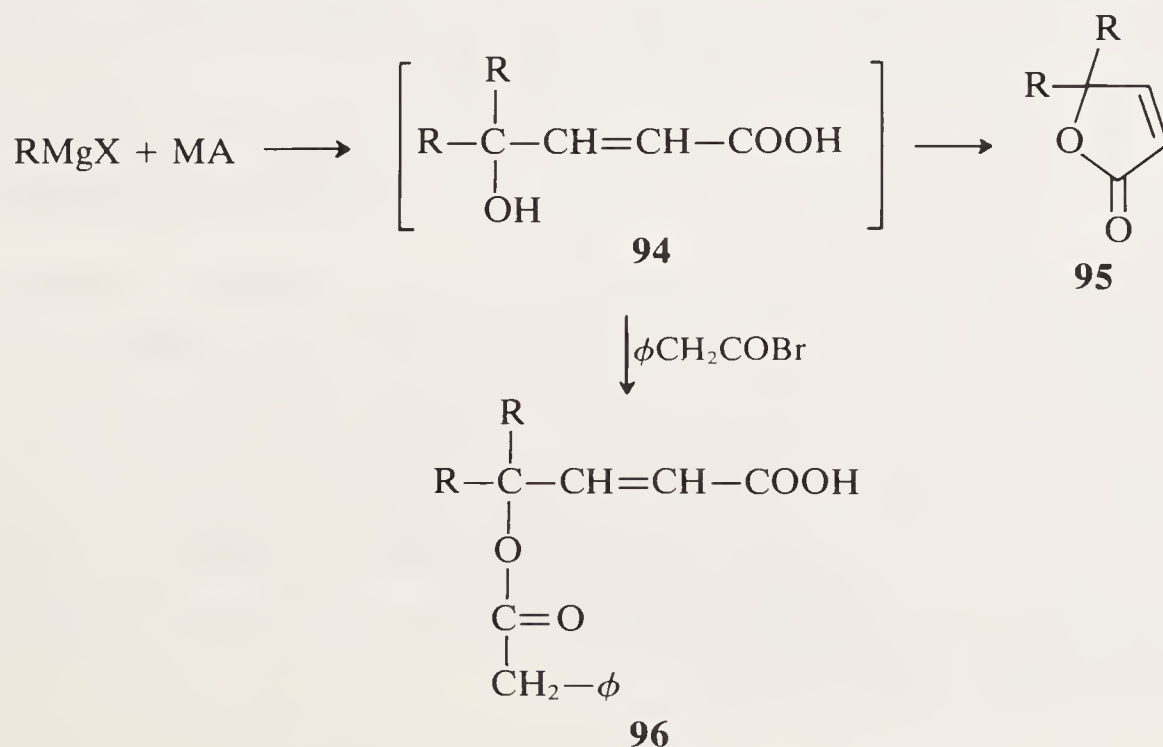


Table 7.4. CuCl-Assisted Reactions of R'MgX with Dialkyl Maleate and Fumarate<sup>a</sup>

R	R'	<i>cis</i> or <i>trans</i>	Reaction condition	% Yield	References
Ethyl	Isopropyl	<i>cis</i>	−10°C	81	67
Ethyl	<i>t</i> -butyl	<i>cis</i>	−10°C	70	67
<i>sec</i> -Butyl	<i>n</i> -Butyl	<i>trans</i>	—	38	68
<i>sec</i> -Butyl	Ethyl	<i>cis</i>	−10°C	57	67
<i>sec</i> -Butyl	<i>n</i> -Propyl	<i>cis</i>	−10°C	63	67
<i>sec</i> -Butyl	Isopropyl	<i>cis</i>	−10°C	81	67, 68
<i>sec</i> -Butyl	<i>t</i> -Butyl	<i>cis</i>	−10°C	74	67

<sup>a</sup> See structure **97**.

on treatment with phenacyl bromide as illustrated using alkylmagnesium chloride as a general reagent. A complex mixture of products were isolated.

The direct reaction of the esters of MA with Grignard and lithium reagents are not very useful, primarily because a mixture of products is formed and the yields are low.<sup>(62,63,69,70)</sup> However, the selectivity to conjugate addition products could be considerably improved using a cuprous chloride-assisted reaction of Grignard reagents with ester derivatives.<sup>(65,66)</sup> Thus, diethyl maleate on treatment with isopropylmagnesium bromide in the presence of cuprous chloride at −10°C gave an 81% yield of the diethyl isopropylsuccinate **97**.<sup>(67)</sup>

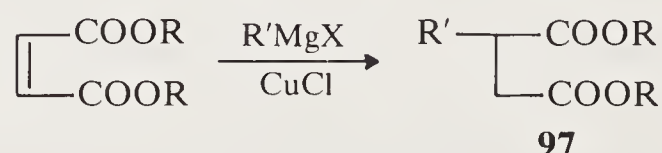
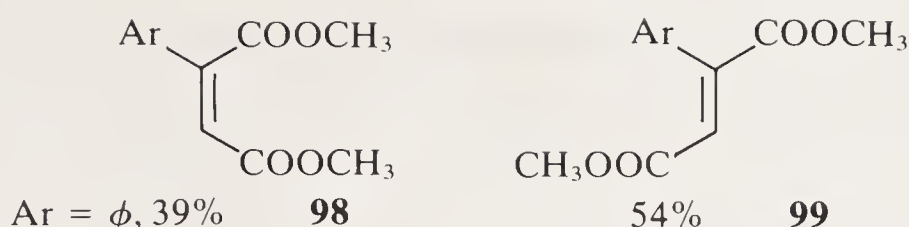


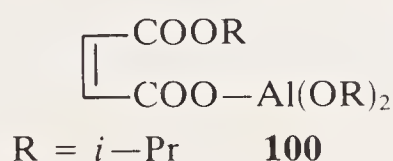
Table 7.4 gives an idea of the range of yields obtainable by cuprous-chloride-catalyzed Grignard reaction. Two reviews discuss the utility and mechanism of the reaction using these reagents.<sup>(67,68)</sup>

Alkyl cadmium halides have been investigated with dialkyl maleate. Marvel *et al.*<sup>(71)</sup> obtained a 29% yield of the conjugate addition product **97** (R = Et, R' = *i*-Pr).

Arylation of dialkyl maleate has been accomplished by Cortese *et al.*<sup>(72)</sup> using a palladium catalyst. On heating an acetonitrile solution of dimethyl maleate, iodobenzene, triethylamine, and 1 mol % palladium acetate at 100°C for 5 h, a high yield of the arylation products **98** and **99** are obtained. Cortese *et al.*<sup>(72)</sup> also reported *p*-aminoiodobenzene giving good yields of the arylation products. This reaction is quite interesting, since arylation is accomplished without the loss of unsaturation. Furthermore, it can be accomplished with catalytic quantities of palladium.



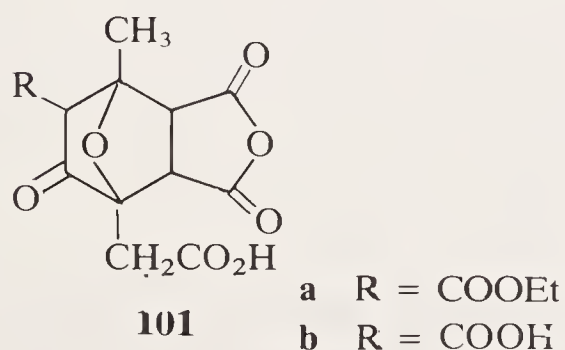
Bulatov and coworkers<sup>(91)</sup> mention a near quantitative yield of an orange solid and propose structure **100** for a product obtained on reacting MA with aluminum triisopropoxide. However, it is not clear why the product **100**, if formed, should be highly colored. Elemental analysis was reportedly performed, but that cannot distinguish between a 1 : 1 charge-transfer complex, which may be colored, and **100**.



It may be apparent that reactions of MA and derivatives with organometallics, either in stoichiometric or catalytic amounts, have a potential of yielding a multiplicity of products, but in some cases selectivities can be controlled to make them potentially useful. The homogeneous catalytic approach involving Pd or copper reagents appears quite promising.

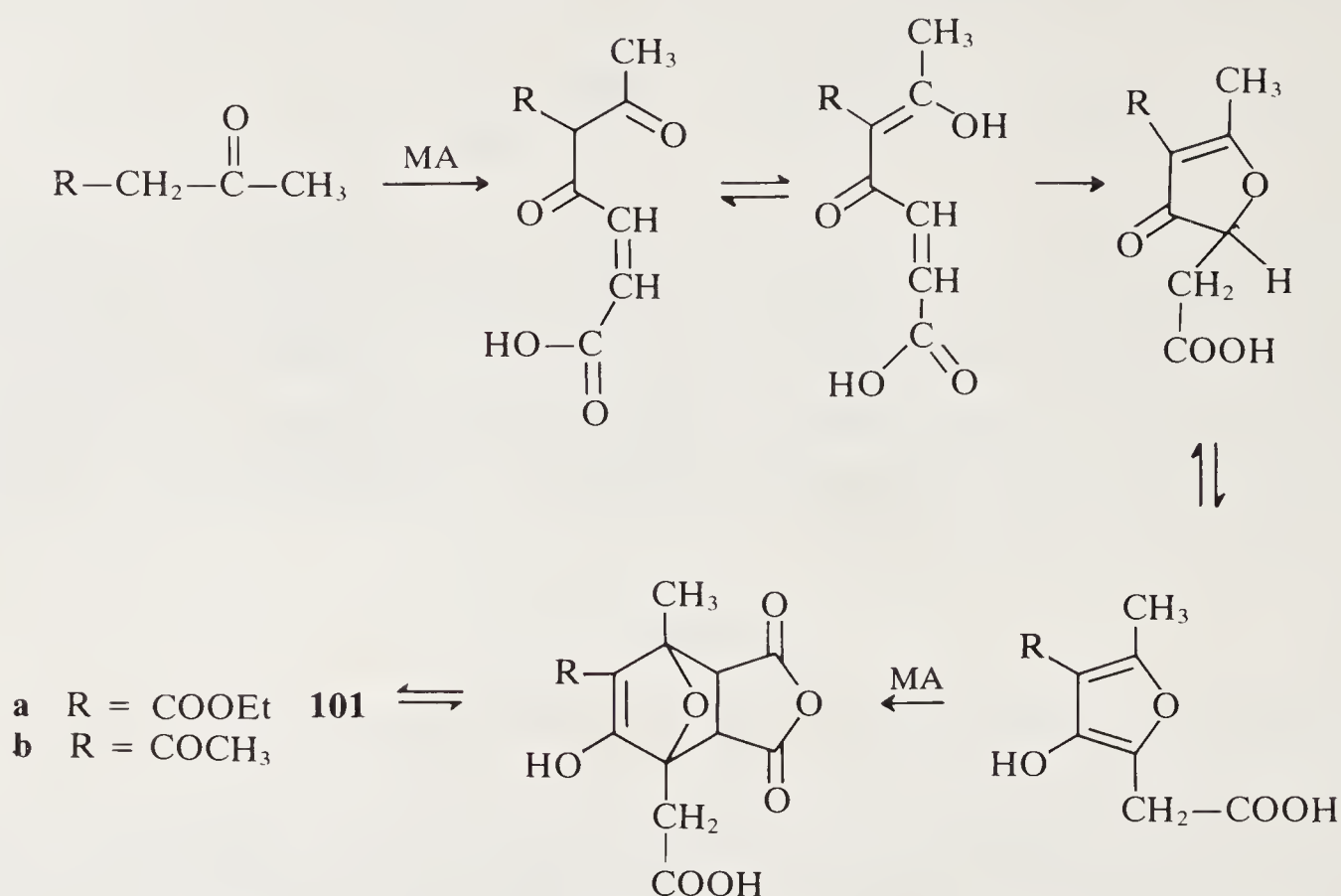
#### 7.4.6. $\beta$ -Dicarbonyl Compounds

Ethyl acetoacetate and acetylacetone react very slowly with MA at room temperature. Over 2–3 weeks, both form an adduct containing 2 moles of MA. Berner<sup>(81)</sup> first examined this reaction in 1946. Acetylacetone gave a 60–70% yield of an adduct **101b**. No yield of the adduct from **101a** was reported. Interpretation of the structure of these products has caused some difficulties.<sup>(81,82)</sup> However, further spectroscopic examination by Bird and Molton,<sup>(83)</sup> as well as Bailey and Stunz,<sup>(84)</sup> Berner and Kolsaker,<sup>(85)</sup> and Krow<sup>(86)</sup> confirm the structure to be **101**.





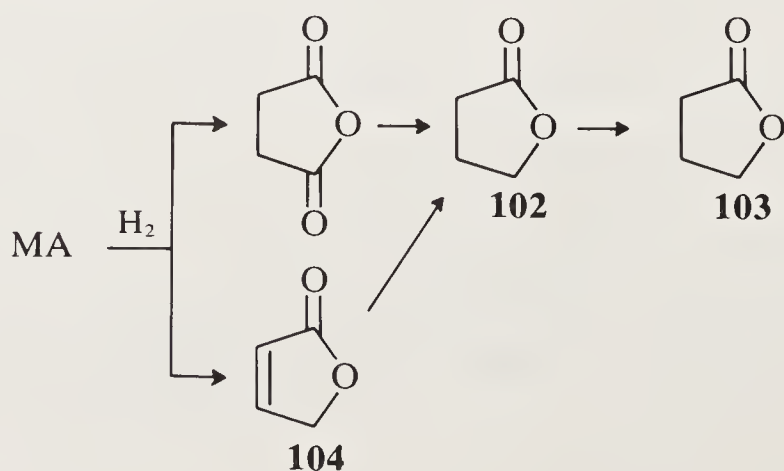
The products of this reaction are proposed to arise as follows<sup>(83)</sup>:



Krow<sup>(86)</sup> has invoked slightly different mechanistic rationalizations involving a Michael addition in the first step. The products of this reaction appear to be very interesting intermediates.

#### 7.4.7. Hydrogenation

In the chapter on olefinic reactions, it was observed that mild hydrogenation of MA produces succinic anhydride (SA). Further reduction of SA can give rise to  $\gamma$ -butyrolactone **102**. This can be accomplished catalytically on a platinum catalyst.<sup>(73)</sup>  $\gamma$ -Butyrolactone **102** can also be further reduced to THF **103**.<sup>(87)</sup> Both these products are commercially significant. In 1976, 83 MM lb of THF were produced in the United States.<sup>(74)</sup> Most of this is derived from acetylene as raw material.  $\gamma$ -Butyrolactone **102** is also a good solvent, intermediate, and monomer, and can be converted to pyrrolidone derivatives.



The last 15 years have seen significant activity in this hydrogenation route, as reflected by patent activity. Mitsubishi in Japan has run pilot plant operation on their catalyst system to achieve 90% overall yield of the products, the proportions of which can be varied significantly at will.

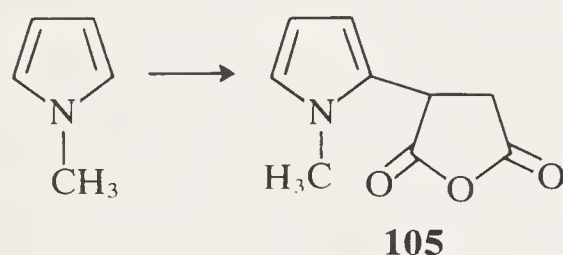
Hakkaido Yuki is believed to be commercially producing THF this way.<sup>(74,75)</sup> This alternative of achieving THF and butyrolactone from MA has the potential for diverting some acetylene chemicals into benzene and C<sub>4</sub>-hydrocarbon-based products.

MA may also be hydrogenated to 1,4-butanediol, a monomer of significant interest for engineering polyesters. Recently, a one-step process giving >90% yield has been claimed.<sup>(99)</sup> A copper chromite catalyst and an alcohol solvent seem necessary.

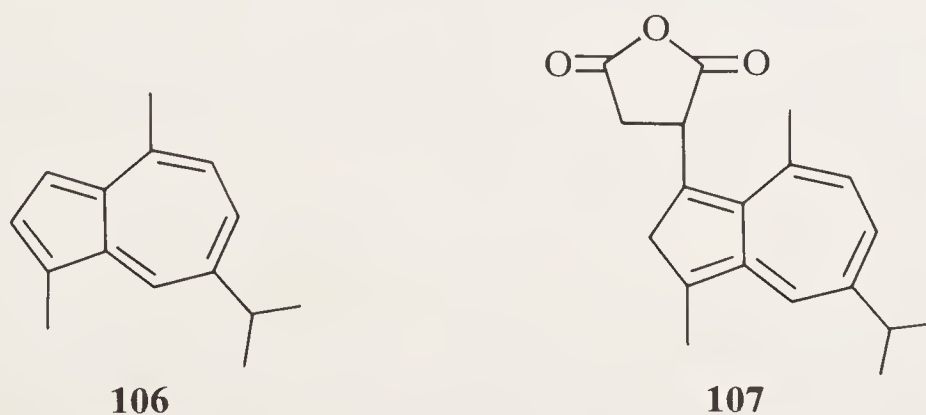
Sodium borohydride reduces MA to 2-buten-4-olide **104** and  $\gamma$ -butyrolactone **102**. If selective, reductions of this type may be of synthetic interest.<sup>(102)</sup>

#### 7.4.8. Alkylation

We observed in Chapter 4 that unlike furan and thiophene derivatives, *N*-alkylpyrroles fail to form a DA adduct. Thus, from *N*-methylpyrrole, an alkylation product **105** is isolated.<sup>(92-94)</sup> Thus electrophilic substitution is the primary course of the reaction. (Also see Chapter 4.)



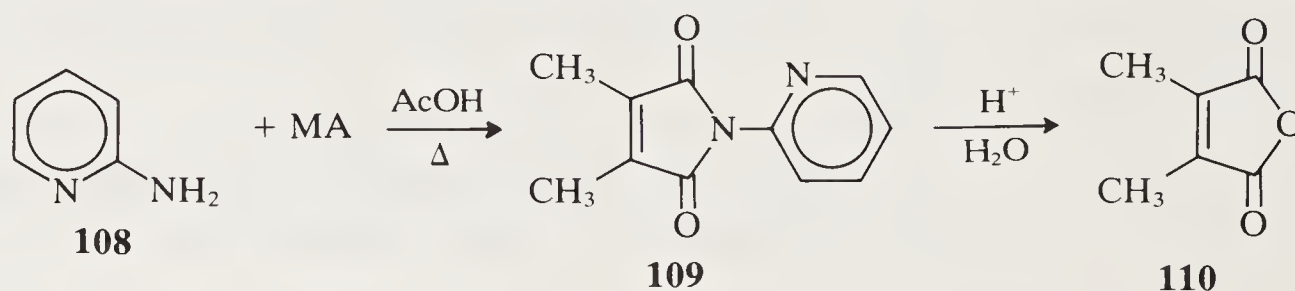
Analogous alkylation of guaiazulene **106** with MA has been reported by Ogura *et al.*<sup>(95)</sup> On refluxing a benzene solution, blue crystalline needles of **107** were obtained. The latter was reported to decompose to the starting



material on heating or during gas chromatography. Ito *et al.*<sup>(96)</sup> have also claimed **107** to be the product. Although the assignment appears chemically reasonable, their labeling studies were inconclusive.

#### 7.4.9. Dimethylmaleic Anhydride Synthesis

An intriguing conversion of MA has been reported by Baumann and Bosshard.<sup>(97,98)</sup> In boiling acetic acid, MA and 2-aminopyridine **108** are converted to a dimethylmaleimide **109** in a 70–80% yield. Other tautomerizable 2-aminoheterocycles were less effective but the reaction was general.



Compound **109** can be easily hydrolyzed to dimethylmaleic anhydride **110**. It was reported that per 2 moles of MA, approximately 1 mole of **109** was produced. One mole of  $CO_2$  was evolved.<sup>(97)</sup> No CO was measured and the fate of the other carboxyl group of MA was not clear. Stoichiometry of the process is not convincing, requiring more hydrogen in the product if 2 MA per product is believed. A detailed study of this interesting reaction appears warranted.

### 7.5. EPILOGUE

In the foregoing, we examined a number of interesting reactions of MA and its derivatives. Most of this chemistry, except for the hydrogenation to THF **103**, is not utilized commercially to any significant extent. Many products obtained in high yields could be useful as intermediates and monomers—arylation using organometallic reagents holds promise in this regard. The reactions themselves, due to their high-yielding nature, may be utilized for polymer grafting and modifications. Novel heterocyclic compounds may also be prepared,<sup>(104)</sup> thus extending the scope of MA's application.



# HOMOPOLYMERIZATION

## 8.1. INTRODUCTION

Maleic anhydride (MA) occupies a unique position in a large family of monomers used to prepare polymeric materials. The simultaneous presence in the molecule of both an electron-acceptor double bond and an anhydride moiety confers unique properties to MA and enables the monomer to be used in both addition and condensation polymerization systems. In fact, one of the largest uses of the monomer, unsaturated polyester resins, employs both moieties for producing the final products (see Chapter 12).

In spite of MA versatility, it was commonly believed and taught until the early 1960s that this monomer would not homopolymerize.<sup>(1-13)</sup> In fact, the reluctance of MA to polymerize was so well known that it was often used as an example to reinforce the concept that steric hindrance, polar effects, etc., retard or prohibit the homopolymerizability of 1,2-disubstituted olefins. This long established thought was shattered in 1961 when it was reported that MA had been homopolymerized.<sup>(14)</sup> Subsequent studies confirmed the discovery and additional studies showed that MA can be polymerized with both  $\gamma$  and UV radiation, in the presence of free-radical initiators, with various pyridine-type bases, electrochemically, and under shock waves.

Poly(maleic anhydride) or the hydrolyzed water soluble polymer has many possible uses, with perhaps the greatest potential application as a detergent builder and scale prevention agent, for water treatment applications. A comprehensive account of MA polymerizations, polymer properties and suggested uses are covered in this chapter. MA-based monomers, such as maleates, fumarates, and maleimides, are also briefly discussed.

## 8.2. POLYMERIZATION METHODS

### 8.2.1. Initiation by $\gamma$ Radiation

Early attempts to homopolymerize MA in the crystalline state with  $\gamma$  ( $^{60}\text{Co}$ ) radiation failed, even after prolonged (100 h) exposure.<sup>(10)</sup> Failures of this type reinforced the concept that MA would not homopolymerize. However, several disclosures offered hints that MA was capable of being homopolymerized. For example, in the early 1930s it was reported that an uncharacterized product obtained from irradiating maleic acid with  $\beta$ -rays

was useful in the treatment of mice with cancer.<sup>(15)</sup> In a paper concerned with heating mixtures of benzoyl peroxide (BPO) and MA, it was postulated that a low-molecular-weight polymer was obtained.<sup>(16)</sup> In a separate paper, using similar conditions, others observed cyclic trimer formation.<sup>(10)</sup> These observations and the report that itaconic anhydride could be homopolymerized<sup>(21)</sup> led Lang *et al.*<sup>(14,22,23)</sup> to believe that MA would homopolymerize. They discovered that the irradiation (<sup>60</sup>Co source) of molten monomer or monomer in acetic anhydride gave polymer in yields up to 98%. Polymerization also occurred in benzene and dioxane but proceeded best in acetic anhydride. In fact, both increased molecular weights and higher yields suggested a synergistic effect in the combination of maleic and acetic anhydrides. Rates of conversion of monomer, as expected, were dependent on dose rate (Table 8.1).

At a constant dose rate, the rate of polymerization was dependent on monomer concentration. In addition, monomer concentration controlled the molecular weight of the polymer. The polymer having an intrinsic viscosity in acetophenone of 0.15 dl/g exhibited a weight average molecular weight of  $23.1 \times 10^3$ . Due to discovery that MA, freed from the restrictions imposed by crystalline habit in the solid form, would homopolymerize,<sup>(22)</sup> many others have discovered and reported other techniques for bringing about the homopolymerization of this monomer.

Heseding and Schneider<sup>(24)</sup> very recently reexamined the homopolymerization of molten MA with  $\gamma$  rays. Their studies were conducted over the 80–150°C temperature range, using <sup>60</sup>Co  $\gamma$  rays with a dose rate of  $10^6$  rads/h. No carbon dioxide was observed during the polymerization. Yields of 14–28% poly(maleic anhydride) were obtained after irradiation for 40 h. This effort confirmed the earlier work.<sup>(22)</sup>

Gamma irradiation of benzene solutions of MA at room temperature, using a 0.1–1.6 Mrads/h dose rate with a total of 26 Mrads, gives approximately a 20% yield of low-molecular-weight polymer or oligomer, a small

Table 8.1. Total Radiation Dose versus Conversion for Polymerization of 1 : 1 Solutions of MA : Acetic Anhydride<sup>a</sup>

Total radiation dose (Mrads) <sup>b</sup>	Conversion <sup>c</sup> (%)	Intrinsic viscosity in acetophenone (dl/g)
1.56	2.69	0.121
4.68	15.11	—
9.36	30.68	0.155
18.36	55.32	—
28.08	61.65	—
39.00	87.08	0.146

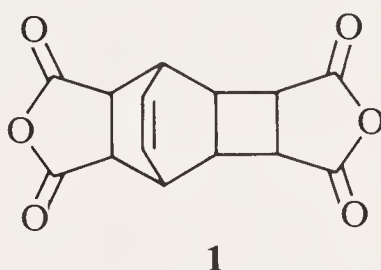
<sup>a</sup> After Reference 22. By permission of John Wiley & Sons, Inc., New York.

<sup>b</sup> Field intensity, 0.195 Mrads/h.

<sup>c</sup> Polymerizations run at 75°C.



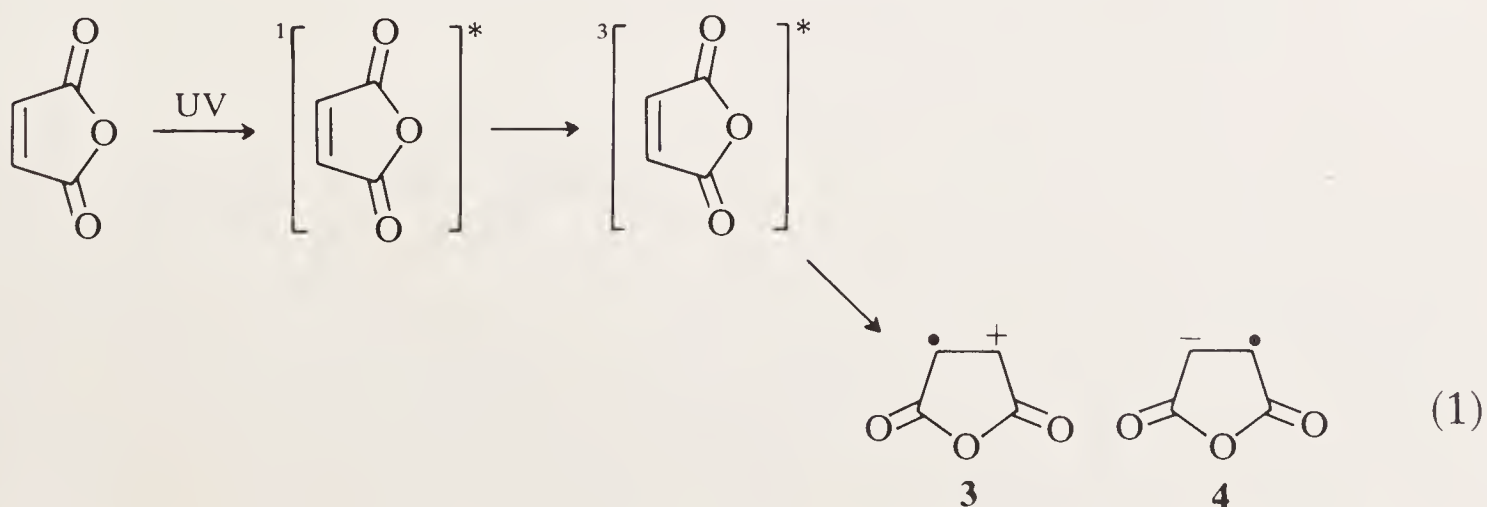
quantity of 2:1 MA–benzene adduct **1** (see Chapter 6), carbon dioxide, carbon monoxide, acetylene, and traces of ethylene and methane.<sup>(25)</sup> A nearly 15-fold change in the dose rate at a nearly constant total dose failed to enhance the yield of MA polymer. This indicates polymerization occurs by way of a short-chain mechanism, i.e., it was characterized by a slow rate of propagation relative to initiation. This is consistent with the known reluctance of MA to undergo homopolymerization. Addition of catalytic amounts of BPO failed to influence the yield of **1** and only slightly improved the yield of polymer. Addition of cyclohexane to the system increased the polymer yield approximately 50% and decreased the yield of **1**. The pale yellow colored polymer, melting with decomposition at 265–295°C, was converted to the methyl ester with methanol and diazomethane, m.p. 82–120°C.



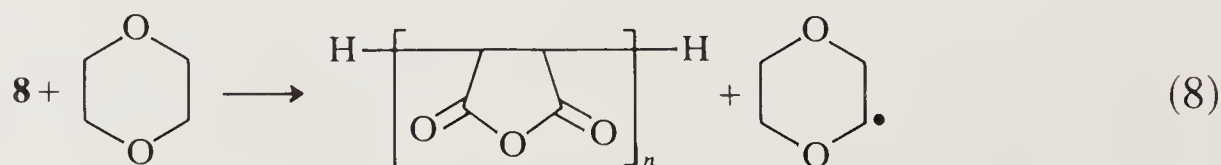
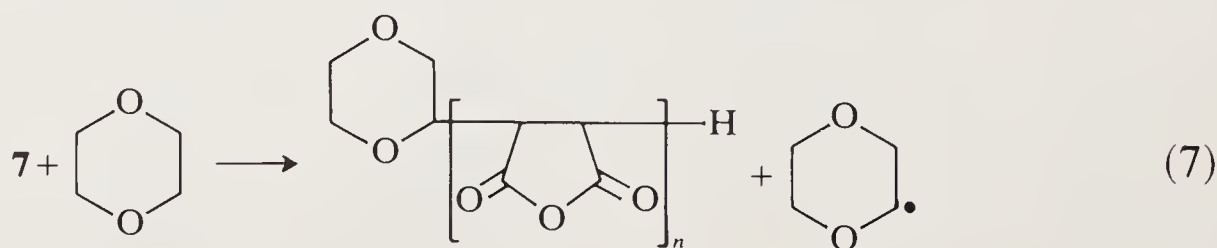
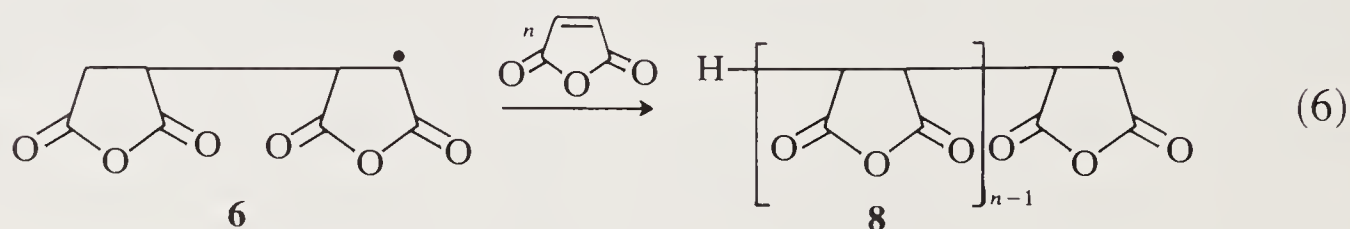
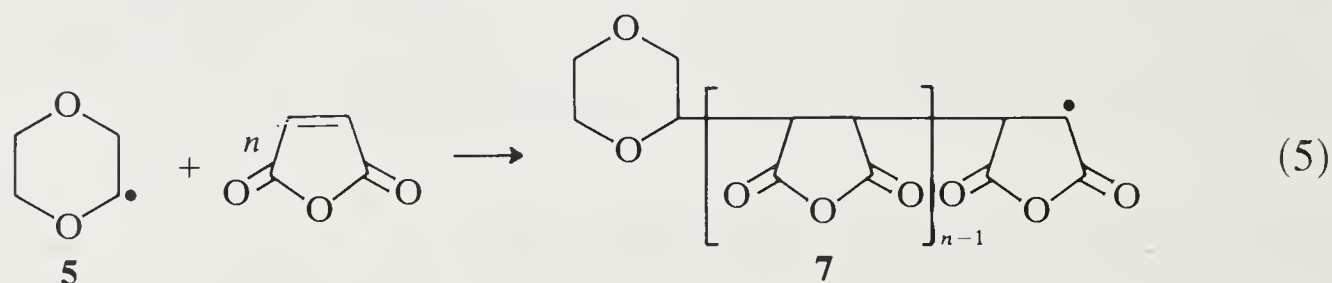
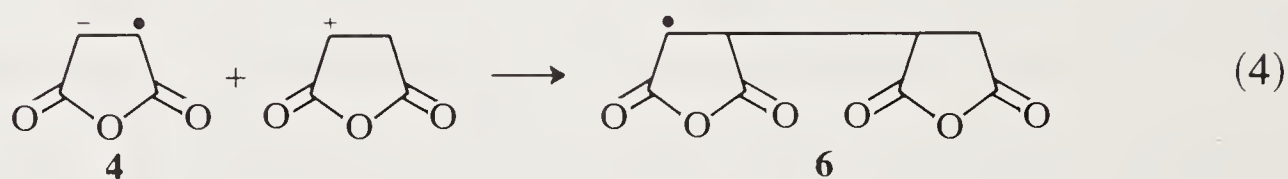
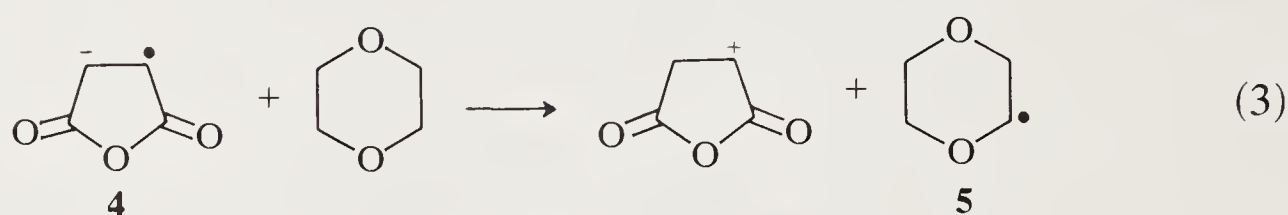
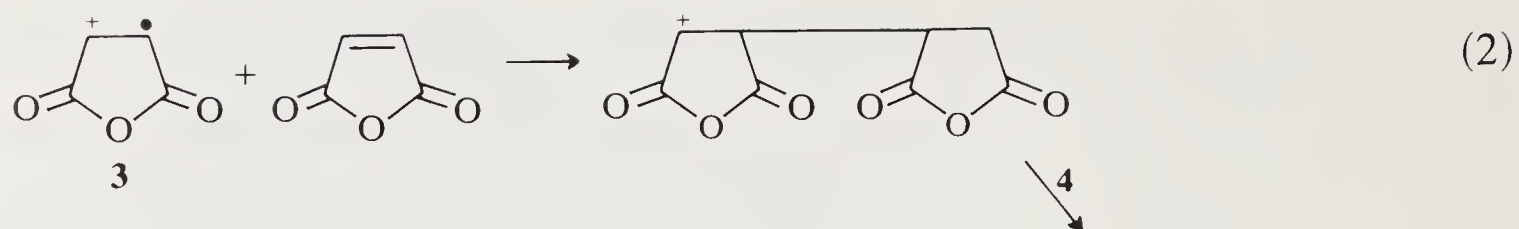
Elemental analyses suggested 2–3 benzene residues were incorporated into the polymer during polymerization. To account for the results, the polymerization mechanism was postulated to involve initiation by phenyl radicals and/or aliphatic radicals when cyclohexane was present. Propagation was thought to consist of copolymerization of MA with either triplet benzene or other excited forms of benzene, such as benzvalene.<sup>(26,27)</sup>

### 8.2.2. Initiation by Ultraviolet Radiation

Irradiation of dioxane solutions of MA gives dimer **2**, accompanied by oligomer containing about four units derived from monomer and one dioxane unit per polymer molecule.<sup>(28–30)</sup> Mass spectroscopy, NMR, IR, elemental, and other analytical studies support a complex reaction mechanism (equations 1–8), consisting of monomer excimer, ionic intermediates, dioxanyl radical, and other intermediates formation during photoexcitation.





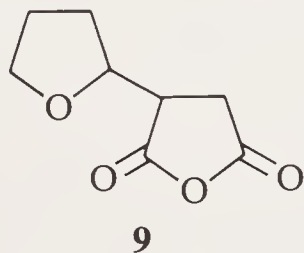


Ionic intermediates in the above reactions are believed to be consistent with other work on electrical conductivity of MA–dioxane solutions where conductivity increases when the mixture is exposed to UV radiation.<sup>(31)</sup> Termination by disproportionation is neglected, since NMR spectra of various oligomers failed to exhibit a vinyl proton for a terminal MA residue.<sup>(29)</sup> An alternate mechanism for dimer and oligomer formation could consist of direct coupling of excited dimer species **3** and **4**.<sup>(32–34)</sup>

Extended exposure of acetic anhydride solutions of monomer to UV light, in the presence of 1% biacetyl, gives polymeric material in about 15% yields.<sup>(14,22)</sup> MA oligomers, containing aromatic residues, have also been obtained from the benzophenone-sensitized photopolymerization of MA in a variety of aromatic solvents.<sup>(35)</sup> These sunlight-induced polymerizations were not inhibited by hydroquinone or *t*-butylhydroquinone.

Maleic anhydride and hexamethylbenzene form a 1:1 charge-transfer complex in methylcyclohexane solvent with a UV maximum at 340  $\mu$ . Ultraviolet irradiation of these solutions brings about the formation of carbon dioxide, pentamethylbenzylsuccinic anhydride, and resinous products (see Chapter 6). Analytical data suggest the polymeric material has a decarboxylated MA building block. Charge-transfer complexes were not detected in solid-state mixtures of MA and pentamethylbenzene.<sup>(25)</sup> Ultraviolet irradiation of these solid mixtures gives cyclic dimer, 1,2,3,4-cyclobutanetetracarboxylic anhydride **2**, and resinous products. Pentamethylbenzylsuccinic anhydride, due to the possible absence of charge-transfer complexes, was not isolated from the solid-state photoreaction.<sup>(25,27)</sup>

For a short time it was believed that UV irradiation of MA in tetrahydrofuran (THF) produced a resinous product.<sup>(36)</sup> Subsequent studies,<sup>(37,38)</sup> however, demonstrated that UV irradiation converted the MA–THF charge-transfer complex into a 1:1 adduct **9** (see Chapter 6).



### 8.2.3. Initiation by Free Radicals

Bartlett and Nozaki<sup>(16)</sup> receive credit as being the first to demonstrate that MA can be homopolymerized with free-radical initiators. In their work, molten monomer was heated (55°C) with 4.58 wt. % BPO to yield an uncharacterized resin having a low degree of polymerization (DP) of ~29. At a reaction temperature of 79.5°C, the product obtained had DP ~25.

They also showed that MA accelerates the decomposition of BPO,<sup>(17)</sup> which could be exploited to enhance the polymerization rate of various other monomers.<sup>(18,19)</sup>

Lang *et al.*<sup>(14,22)</sup> also attempted to polymerize molten MA at 60–67°C with 1% lauroyl peroxide or azobisisobutyronitrile (AIBN) but obtained only trace amounts of polymer. In the presence of 5.0 wt. % BPO, either in the melt at 60°C or in acetic anhydride at 70°C, the yield of polymer was approximately 34%. The solution polymer, having an intrinsic viscosity in acetophenone of 0.12 dl/g, exhibited a 320°C (dec.) melting point.

Kinetic studies of the BPO-initiated polymerization of MA in the melt at 74.5°C showed maximum conversion of 30–40%, even when peroxide concentrations exceeded 10 wt. %.<sup>(39)</sup> The BPO concentration for six polymerizations were varied from 2.65 to 10.70 wt. %. The average heat of polymerization ( $-\Delta H$ ), determined calorimetrically in bulk was discovered to be approximately  $18.3 \pm 1.9$  kcal/mol. Extrapolation to zero, on the plot of initiator wt. % versus heat of polymerization, gave an initiator-free value for  $-\Delta H$  of 14.3 kcal/mole. This suggests the ceiling temperature for MA would be quite favorable for polymerization. Chain transfer to monomer was considered to play a dominant role in the polymerization. Intrinsic viscosities in 2-butanone of 0.05–1.0 dl/g and ebulliometric molecular weight determination showed the average degree of polymerization ( $\overline{DP}$ ) to be about 4–11. Analytical studies failed to show initiator fragments in the polymer and caused Joshi<sup>(39)</sup> to suggest that the initiating species consisted of secondary radicals derived from the monomer by chain-transfer reaction.

The radical homopolymerization of MA has also been investigated in benzene at 70°C, using lauroyl peroxide, to determine kinetics for the reaction.<sup>(40)</sup> The reaction order versus monomer and initiator concentration, as well as the activation volume, give strong support for polymerization with degradative transfer to monomer, thereby confirming Joshi's<sup>(39)</sup> results. The kinetic results fit the Deb<sup>(41)</sup> equation and confirm the abnormal character of the polymerization. Kellou and Jenner<sup>(40)</sup> find the enthalpy and entropy values for the polymerization to be, respectively,  $-\Delta H \approx 14$  kcal/mol and  $-\Delta S \approx 30\text{--}35$  kcal K<sup>-1</sup> mol<sup>-1</sup>, comparable to other vinyl polymerizations. A plot of temperature versus rate of polymerization showed a ceiling temperature of approximately 150°C, which is low for the reported entropy value.

Others have also looked at the kinetic characteristics of the solution homopolymerization of MA, using benzene, dioxane, and acetic anhydride solvents with BPO initiator.<sup>(42)</sup> In dioxane, polymerization rates are proportional to initiator concentration to the  $\frac{1}{2}$  power, supporting a recombination mechanism for termination of the kinetic chains.<sup>(42)</sup> Reminiscent of the  $\gamma$ -radiation polymerization systems,<sup>(22)</sup> an increased rate of polymerization and greater molecular weight is observed in acetic anhydride solvent. All evidence supports the assumption that acetic anhydride is not a "pure" solvent for the



polymerization mixture but a solvent with both great solvating power and strong tendency to form molecular complexes, i.e., charge-transfer complexes, with the monomer molecule.<sup>(42)</sup>

Higher molecular weights and much improved conversions are achieved by the incremental addition of BPO or di-*t*-butyl peroxide to molten MA at temperatures  $\geq 80^{\circ}\text{C}$ .<sup>(43)</sup> Thus, 1 wt. % of initiator was initially added and the molten mixture heated at  $85\text{--}90^{\circ}\text{C}$ . Even though heat was terminated, the exothermic reaction caused the temperature to rise in a short time (1–20 min) to as high as  $150^{\circ}\text{C}$ . After cooling to  $110\text{--}130^{\circ}\text{C}$ , additional initiator was added in 3 to 5 successive increments of 1 wt. % at 30-min intervals. Yields increased from about 20% with the initial 1% to about 80% with the sixth addition of 1% initiator. Even though the total initiator concentration was about the same as in other studies, incremental addition clearly gives improved yields in a shorter reaction time. Light-scattering studies were claimed to show molecular weights in excess of 30,000 and as high as 94,000, a definite improvement over previous results.

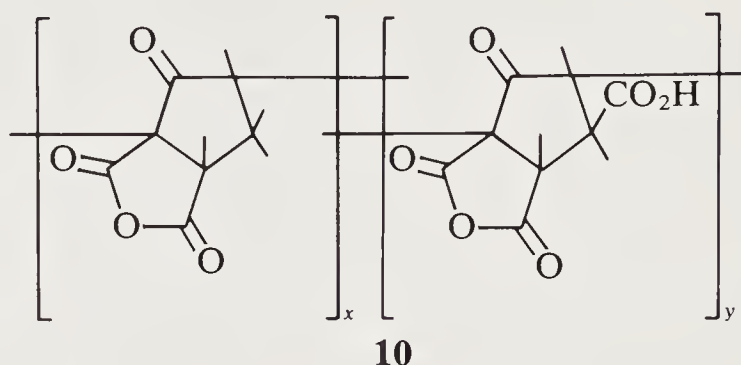
Steady or dropwise addition of a benzene solution of diisopropyl percarbonate initiator, over an 8-h period, to a solution of MA in benzene at  $75^{\circ}\text{C}$  and subsequent additional heating at  $75^{\circ}\text{C}$  for 2 h gave an 85% yield of crude poly(maleic anhydride).<sup>(44)</sup> Other initiators, such as BPO, dicyclohexyl percarbonate, or dilauryl peroxide, solvents and solvent mixtures, and accelerators to speed decomposition of the principle free-radical initiators were also studied and claimed to give improved results.

Attempts to polymerize MA with 1 wt. % BPO in toluene at  $60^{\circ}\text{C}$  and  $90^{\circ}\text{C}$  and under 4900 atm gave low yields (20–70%) of dimer, depending on reaction temperature.<sup>(45)</sup> Using toluene solvent, others observed good results with dropwise addition of BPO initiator and running the polymerization for ca. 5 h at  $90\text{--}95^{\circ}\text{C}$ .<sup>(46)</sup>

Essentially quantitative yields of poly(maleic anhydride) are obtained by the use of 2–6 wt. % acetyl peroxide in molten MA at temperatures of  $85\text{--}135^{\circ}\text{C}$ .<sup>(47)</sup> During polymerization copious amounts of carbon dioxide are eliminated and polymers, free from color, are obtained with molecular weights of 3500–7500. It is significant to note that the patent<sup>(47)</sup> discloses that polymers with cryoscopic molecular weights of 300–1000 are equivalent to light-scattering molecular weights up to 50,000. It is possible that if the same analytical procedures were used in all the studies one would find all polymers prepared by free-radical initiators have comparable molecular weights.

Other reports also claim that carbon dioxide is eliminated during free-radical-initiated homopolymerizations of MA.<sup>(48,49)</sup> In these two studies, monomer was polymerized in either benzene, toluene, decalin, chloroform, or acetic anhydride with 5 mol % AIBN at  $70^{\circ}\text{C}$ , BPO at  $70\text{--}110^{\circ}\text{C}$ , lauroyl peroxide at  $60\text{--}70^{\circ}\text{C}$ , dichlorobenzoyl peroxide at  $70^{\circ}\text{C}$ , and diisopropyl percarbonate at  $75^{\circ}\text{C}$ . Redox systems, such as dimethylaniline-diisopropyl

percarbonate and triisobutylboron oxygen were ineffective as initiators at 20°C.<sup>(48)</sup> Investigation of the carboxylic acid group content, elemental analyses, and infrared and nuclear magnetic resonance spectroscopy data caused the authors<sup>(48)</sup> to suggest a mechanism of simultaneous polymerization and decarboxylation to give a polymer with structure **10**.



Maleic anhydride oligomers of molecular weight 440–725, prepared in xylene solvents, are liquid at temperatures  $>45^{\circ}\text{C}$ . The resins are reported to be obtainable in high yields by oligomerization of the monomer in *o*-xylene, using *tert*-butylperoxide initiator.<sup>(50)</sup> A highly useful procedure also employs mixed solvents containing *o*-xylene, polymerization temperatures of 120–145°C, and di-*tert*-butyl peroxide initiator.<sup>(51)</sup> Polymer yields are substantially enhanced where the *o*-xylene is replaced by an amount of monochlorobenzene such that the ratio of monochlorobenzene to xylene is from 1:1 to 10:1 by weight.<sup>(252)</sup>

Considerable work has been done at the FMC Corporation<sup>(52–55)</sup> on the free-radical-initiated homopolymerization of MA. In their first patent,<sup>(52)</sup> they claim that molten MA or MA in the presence of solvent, may be treated with 0.5–2.0% hydrogen peroxide to form the corresponding peracid (see Chapter 3). After addition of a stoichiometric amount of an acylating agent, the reaction mixture is heated 4–6 h at 65–95°C to obtain good yields of the desired polymer. Addition of boric acid to these polymerization systems aids in obtaining light-colored material.<sup>(53)</sup> Others have shown that production of the acid polymer is facilitated by admixing MA dissolved in 1–5  $\times$  molar amount of acetic anhydride with 0.2–0.5  $\times$  molar amount of hydrogen peroxide and simultaneously heating to 80–140°C.<sup>(254)</sup> It has also been shown that peresters derived from MA in this fashion are very useful for curing acrylate monomer–polymer syrups.<sup>(257)</sup>

High yields (94%) of polymer are also obtained by adding a preheated (40–45°C) solution of monomer, diacetyl peroxide, and chlorobenzene, over 2.5 h, to chlorobenzene at 105–111°C and subsequent heating for 1 h at 105°C.<sup>(54)</sup> In another procedure,<sup>(55)</sup> white powdered polymer, free of monomer, is manufactured with little evolution of heat by charging a heated feed solution of monomer, solvent, and initiator into a heated reaction zone containing monomer and inert solvent. The polymer, which precipitates during the course of the reaction, is easily collected, washed, and dried.



It is well known that oxygen inhibits the homopolymerization of vinyl-type monomers. Poly(maleic anhydride) is also best obtained when oxygen is excluded from polymerization solutions of MA and peroxide initiators.<sup>(56)</sup> Substantially colorless polymer is obtained when both oxygen and UV light are excluded.<sup>(57)</sup>

The homopolymerization of MA is difficult under conditions commonly used for vinyl monomers. The comparatively low reactivity of MA to the initiator or polymeric free-radicals can be correlated with the high value for the Alfrey–Price<sup>(58)</sup>  $e$  value of 2.25 for the unsaturated anhydride (see Chapter 9).<sup>(59)</sup> Complete conversion of monomer calls for fairly large quantities of initiator. An exception occurs when a conventional amount of an initiator is added slowly to molten MA at temperatures at which the initiator half-life is  $<1$  h, preferably  $<30$  min.<sup>(60)</sup> Using *tert*-butyl-peroxypivalate and di-*sec*-butyl-peroxydicarbonate to illustrate this concept, it was shown that conversions increased with temperatures or decreasing half-life of the perester initiator. These and other observations led Gaylord and coworkers<sup>(60,61,276)</sup> to advance the concept that while MA will not polymerize per se, excited MA readily undergoes polymerization. Thus, propagation is advanced by either excited monomer or excited dimer, resulting from the reaction of the excited monomer with the ground-state monomer.

Transfer of excitation energy from reactions of initiator decomposition products, resulting from short addition times and temperatures producing very short initiator half-life, was previously advanced to explain copolymerization of conjugated dienes with MA to give 1:1 copolymers (see Chapter 10).<sup>(62,63)</sup> Diels–Alder products normally form from the diene–MA ground-state charge-transfer complex (see Chapter 4). However, with peroxide initiators or ultraviolet light in the presence of photosensitizers, the ground-state charge-transfer complex (CTC) is excited and polymerized. Furthermore, it is believed that the excited CTC is the reactive species which undergoes addition to the propagating chain.<sup>(60,61)</sup>

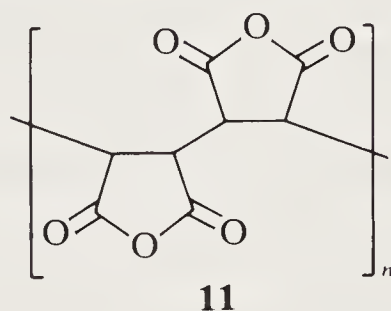
Enhanced absorption and emission lines are detected in the NMR spectra of peroxides and azo compounds subjected to rapid decomposition.<sup>(71)</sup> This phenomenon, referred to as chemically induced dynamic nuclear polarization (CIDNP), was first detected during the free-radical-initiated homopolymerization of MA.<sup>(64,65)</sup> CIDNP does not arise in reactions where radical transfer is the only step but is especially evident where strong monomer–radical pairs exist and where termination steps prevail.<sup>(65)</sup>

The presence and participation of excited charge-transfer complexes or species was confirmed by carrying out peroxide-induced homopolymerization of monomer in the dark with the presence of various photosensitizers.<sup>(60)</sup> Adding 2 mol % of *tert*-butylperoxypivalate over a 10-min period at a reaction temperature of 80°C gave yields ranging from 40%, with no sensitizer, to 62.5% in the presence of sensitizers having triplet energies from



68–85 kcal/mol. Of the ten sensitizers studied, benzophenone appeared to give the best results. Yields were lower in the case where triplet energy values were  $<68$  kcal/mol, suggesting these materials were acting to quench the concentration of polymerizable species (excimers). Molecular weights were also reduced by quenchers such as anthracene, naphthalene, and 1'- and 2'-acetophenones. Thus, failure to effectively polymerize MA with radical initiators, under conventional conditions, could possibly be attributable to insufficient concentration of polymerizable excimers.<sup>(60)</sup> High concentrations of radicals, generated by rapid decomposition of an initiator<sup>(22,48)</sup> as well as  $\gamma$ <sup>(22)</sup> and photosensitized ultraviolet radiation,<sup>(35)</sup> appears to provide good conditions for proper excitation.

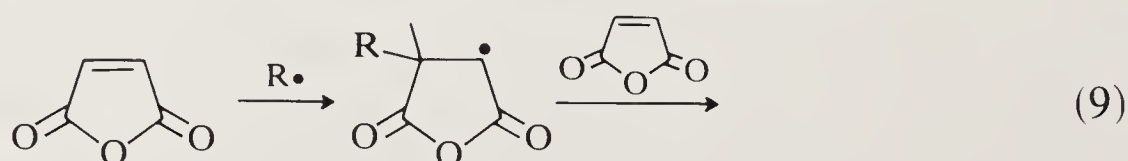
Homopolymers of MA would be expected to have a carbon–carbon backbone, resulting from double-bond additions **11**. In most cases reported,

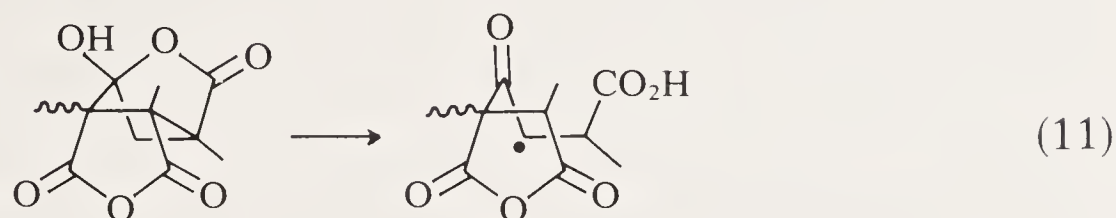
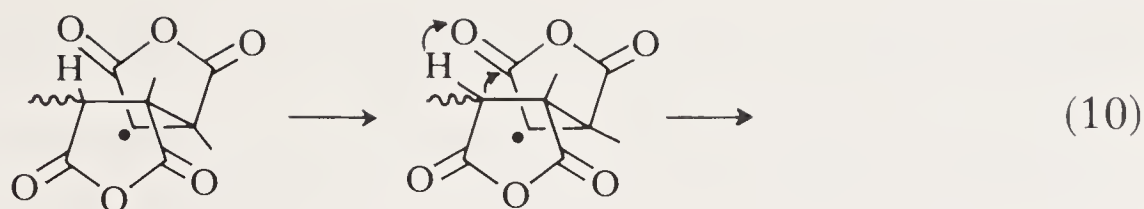


elemental analyses have failed to correspond to the expected empirical formula,  $C_4H_2O_3$ . Even where carbon dioxide evolution was not detected, such as in the photosensitized polymerization of monomer under sunlight,<sup>(35)</sup> the resultant polymer was high in carbon and hydrogen and deficient in oxygen. This has caused some authors to speculate that the analytical data were consistent with a decarboxylated material.

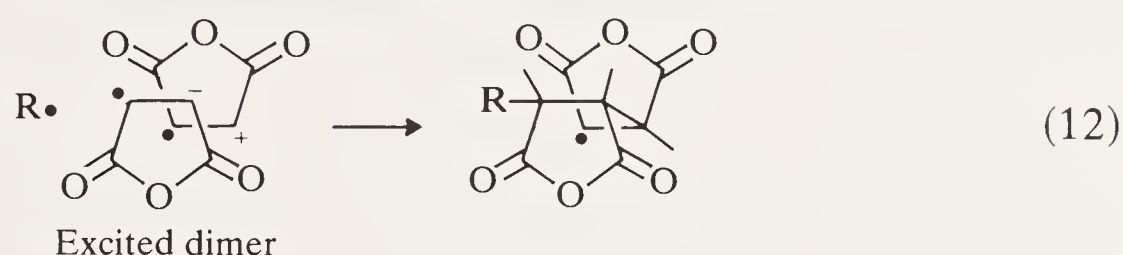
Carbon dioxide has also been detected during the AIBN-initiated polymerization of MA.<sup>(48)</sup> Since the polymer suffers some decarboxylation at elevated temperatures, it was originally believed that carbon dioxide evolved from the polymer formed as a result of polymerization.<sup>(66)</sup> Braun *et al.*<sup>(48)</sup> suggested the analytical data support the concept that loss of  $CO_2$  occurs simultaneously with and as part of the polymerization process. Polymers formed under this assumption are presumed to contain units of succinic anhydride and cyclopentanone rings **10**.<sup>(45,49)</sup>

A reaction sequence consisting of the addition of two MA molecules followed by proton transfer from the penultimate to the ultimate moiety (reactions **9–11**), was envisioned to account for structure **10**.<sup>(48)</sup> Decarboxylation of the cyclopentanone residue results in a decreased functionality.





The proposed participation of excited species in the propagation step is believed by Gaylord *et al.*<sup>(60,276)</sup> to be consistent with the above mechanism, assuming excited MA dimers are the polymerizing species [Eq. (12)]:



The above reaction mechanism, leading predominantly to cyclopentanone structures, can only be considered as highly unconventional and without precedent in organic or polymer chemistry. Bacsikai<sup>(67)</sup> recognized this and investigated the validity of this unusual polymer structure. This study clearly established that, even if one assumes all of the CO<sub>2</sub> eliminated came from the MA molecule, the extent of decarboxylation in peroxide-initiated polymerizations is minimal. Simple calculations show that poly(maleic anhydride) prepared with 1% BPO or 2% di-*tert*-butyl peroxide contains less than 4.7 or 2.5 mol % decarboxylated MA, respectively. Thus, any deviations from the normal poly(maleic anhydride) structure **11**, if any at all, must be very minor and do not have the claimed polycyclopentanone structure. In the absence of retained solvent, the NMR spectra of the isolated polymers fail to show CH<sub>2</sub> group resonance, required by the cyclopentanone ring. Regel and Schneider,<sup>(278)</sup> with their recent <sup>1</sup>H and <sup>13</sup>C Fourier-transform NMR studies, have shown that MA polymer prepared with both peroxide and <sup>60</sup>Co radiation (10<sup>5</sup> rads/h) have the poly(2,5-dioxotetrahydrofuran-3,4-diyl) structure. Also, elemental analysis and methoxy content of the esterified polymer was in good agreement with esterified **11**. Thus, poly(maleic anhydride), prepared with peroxides, cannot be significantly decarboxylated and must have essentially structure **11**.

It was recently shown that poly(maleic anhydride) may contain trapped radicals, when formed by the polymerization of monomer in the presence of BPO or AIBN at 60°C.<sup>(70)</sup> The molecular weight of the polymers, obtained in low yields after 20 h in the presence of 2–10 mol % initiator and

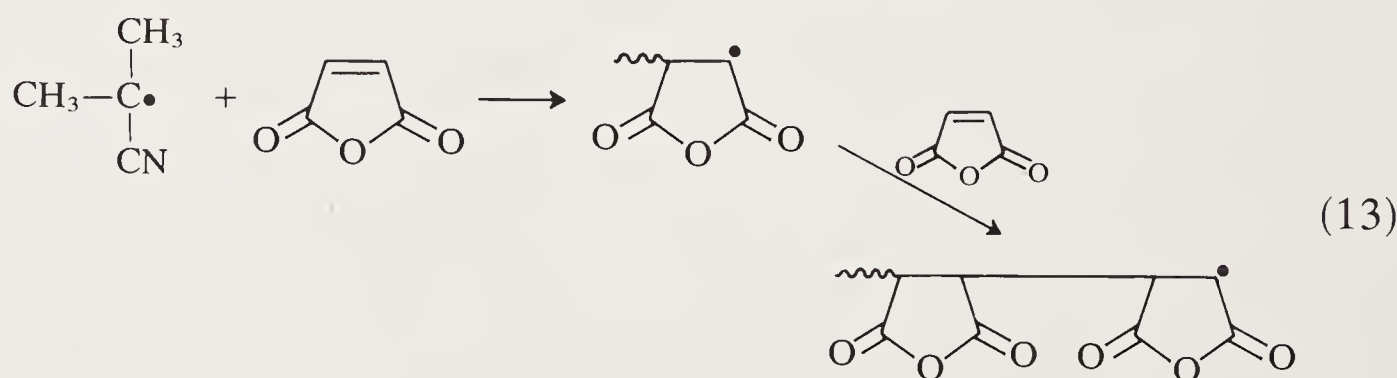


dichloromethane or benzene solvents, were shown by the ebulliometric method to be in the range of 500–1000.

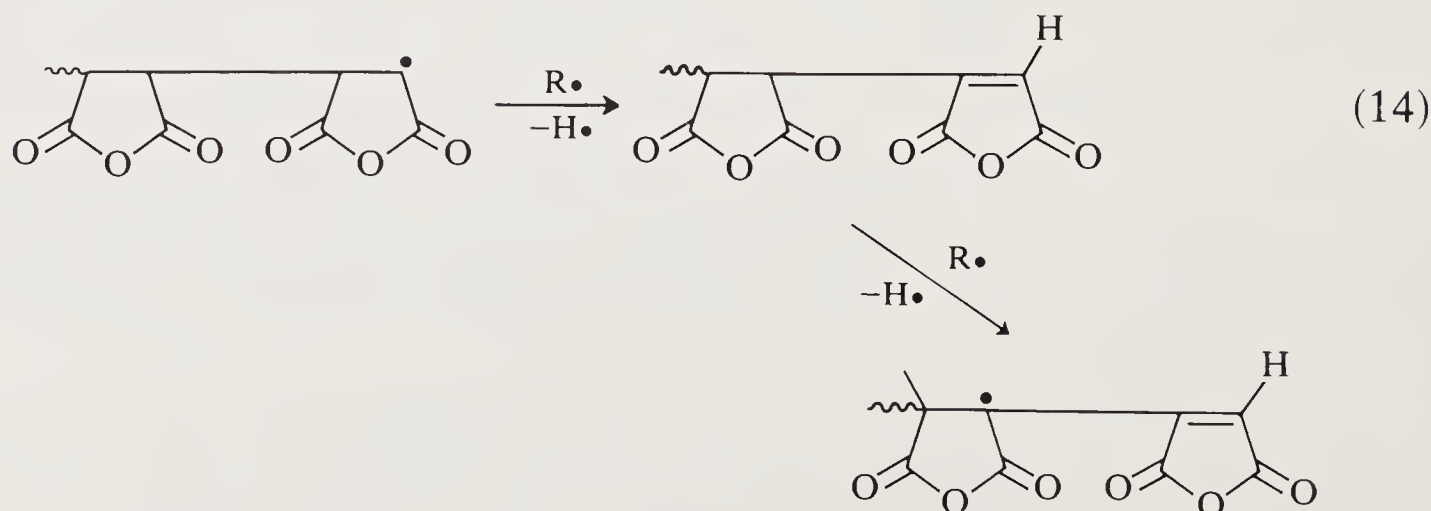
Three different types of radicals were identified by electron spin resonance (ESR) spectroscopy. In the first case, isolated poly(maleic anhydride) contained one radical identifiable as the MA propagating radical. This same radical was shown to be capable of polymerizing styrene and copolymerizing styrene–methyl methacrylate mixtures. It was also shown that the two other radicals were transformed into active species capable of the cationic polymerization of isobutyl vinyl ether or vinyl ethers in the presence of monomeric MA.<sup>(70,71)</sup>

Low yields, in the radical-initiated polymerization of MA, are attributed to suppression by the strong electrostatic repulsion between monomer and monomer radical in each step of the polymerization. Initiator radicals which have the same electropositive charge would have only a very small tendency to attack the MA monomer double bond. It is also suggested that the MA radical always has one readily replaceable hydrogen, resulting in the formation of a conjugated polymer system.<sup>(70,71)</sup> This monomer characteristic also makes for difficulty in polymerizing MA.

The mechanism for trapped radicals and polymer formation, with AIBN initiator,<sup>(70,71)</sup> has been envisioned as follows [Eq. (13)]:



Conjugated radicals presumably occur when initiator radicals interact to eliminate hydrogen [Eq. (14)]:

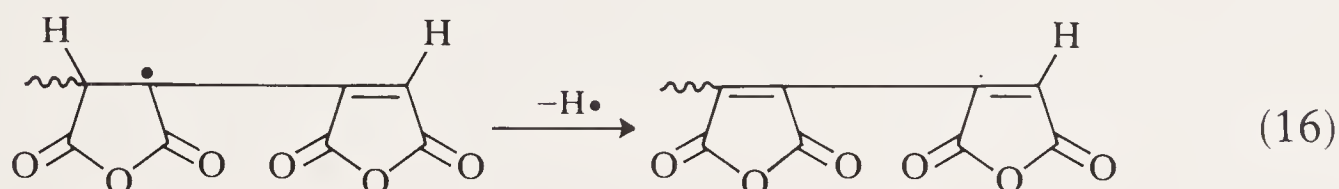
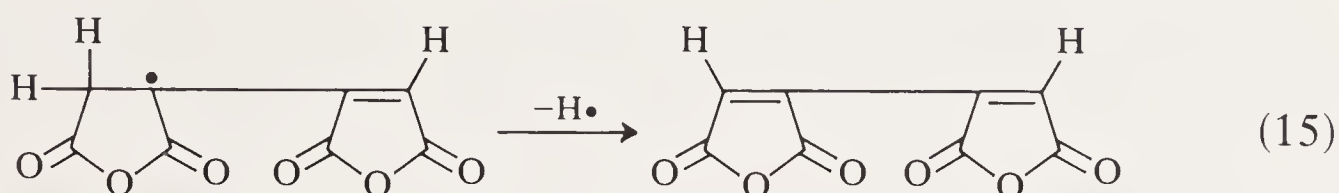


In contrast to the BPO radical, AIBN radicals should exist more freely in solution because of the difficulty of the attack on MA and weak affinity

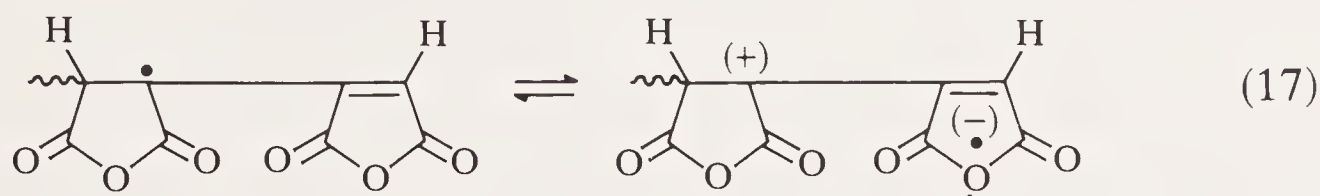


for the hydrogen atom. Also, the propagating MA radical, due to electrostatic repulsion, hardly attacks MA.

Due to the electrophilic nature of the MA residue, conjugated unsaturation may be brought about by the release or abstraction of additional hydrogen atoms [Eqs. (15) and (16)].

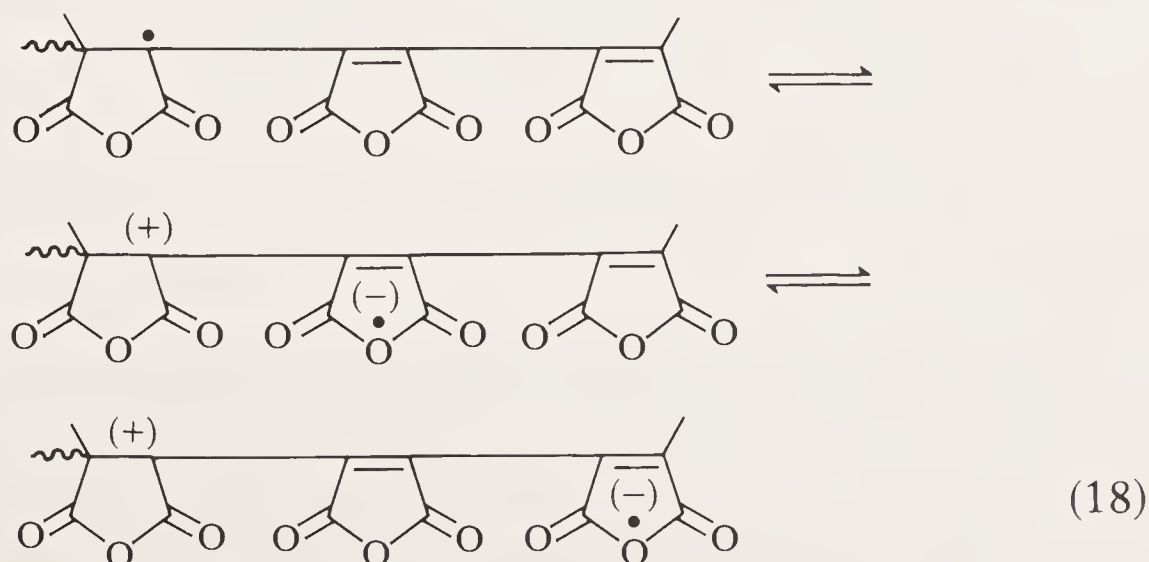


The unpaired  $\pi$  electron in the conjugated radical is thought to be delocalized in the MA ring, giving a resonance structure capable of initiating cationic polymerization [Eq. (17)].

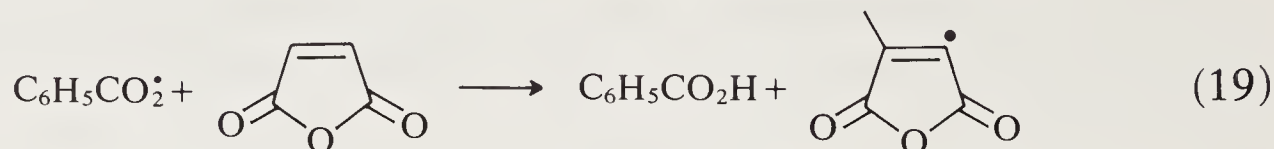


A similar type cationic moiety is claimed in the polymerization of olefin oxides initiated by radical initiators in the presence of MA, i.e., the conjugated radical of poly(maleic anhydride) is the active initiating moiety in the cationic polymerization of the epoxide.<sup>(72)</sup>

In the extended conjugated radical, the unpaired  $\pi$  electron could be strongly attracted by high electron affinity, i.e., two unsaturated anhydride rings, so that such an electron seems to be trapped in the polymer. This type structure gives a very narrow ESR spectrum [Eq. (18)]:

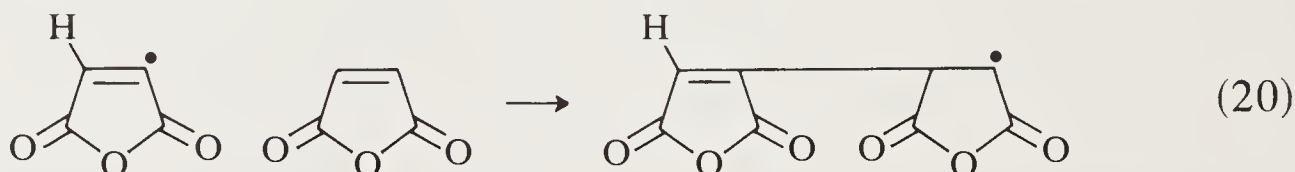


In contrast to AIBN, initiation by BPO radicals involves hydrogen abstraction from monomer to yield a monomer radical [Eq. (19)]:

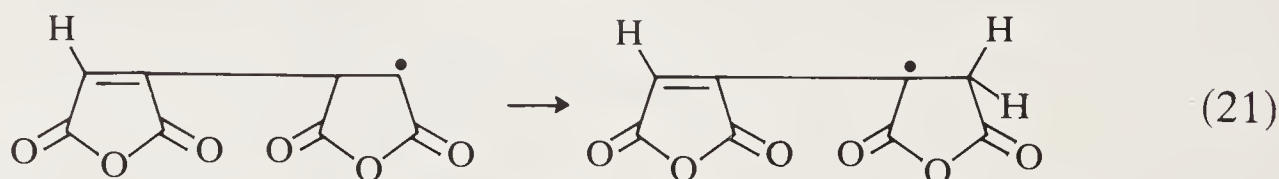


High hydrogen affinity enables the BPO radical to abstract a hydrogen from the MA monomer. As shown, the radical hardly attacks the double bond due to electron repulsion.

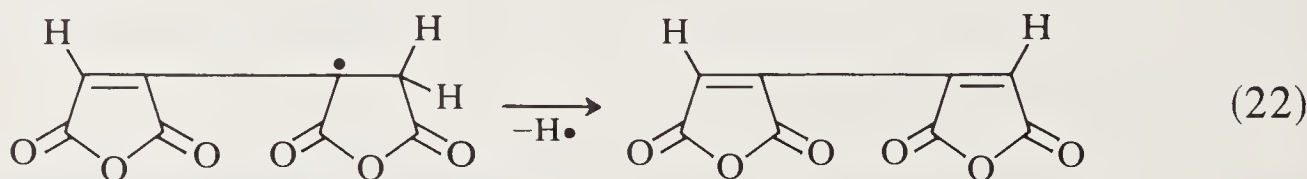
Monomer radicals add monomer to give dimer radicals and a polymer [Eq. (20)]:



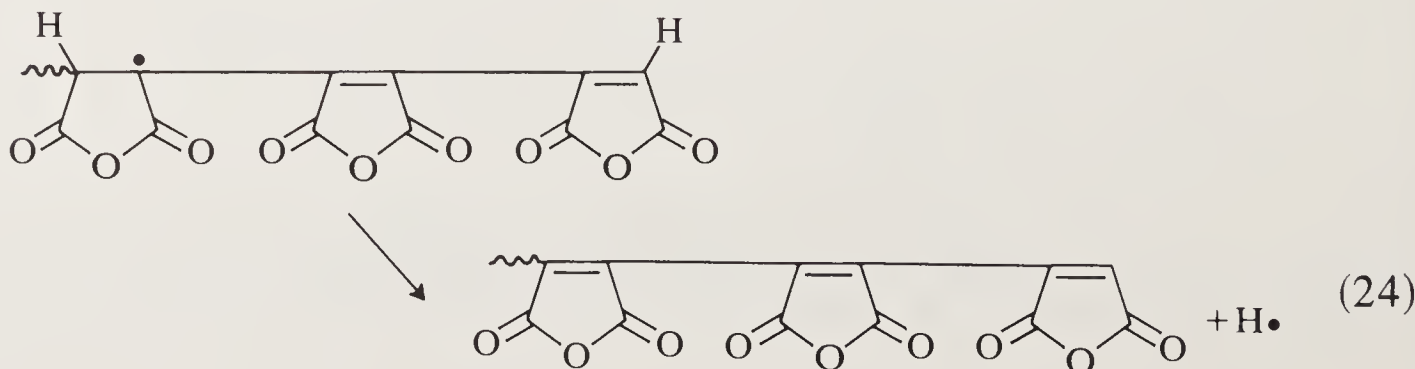
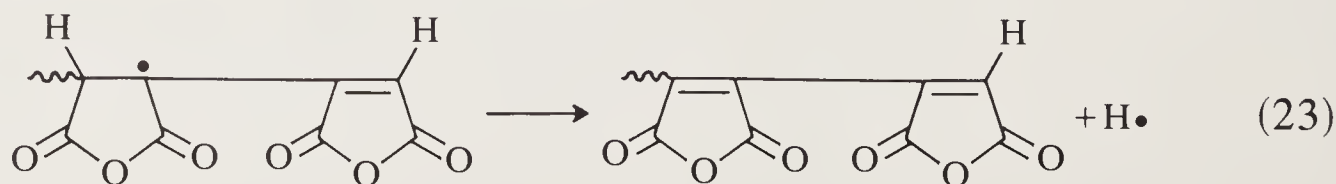
Due to an unpaired electron, carbonyl, and maleoyl residue influences, the mobility of the hydrogen moiety in the dimeric radical brings about a conjugated radical [Eq. (21)]:



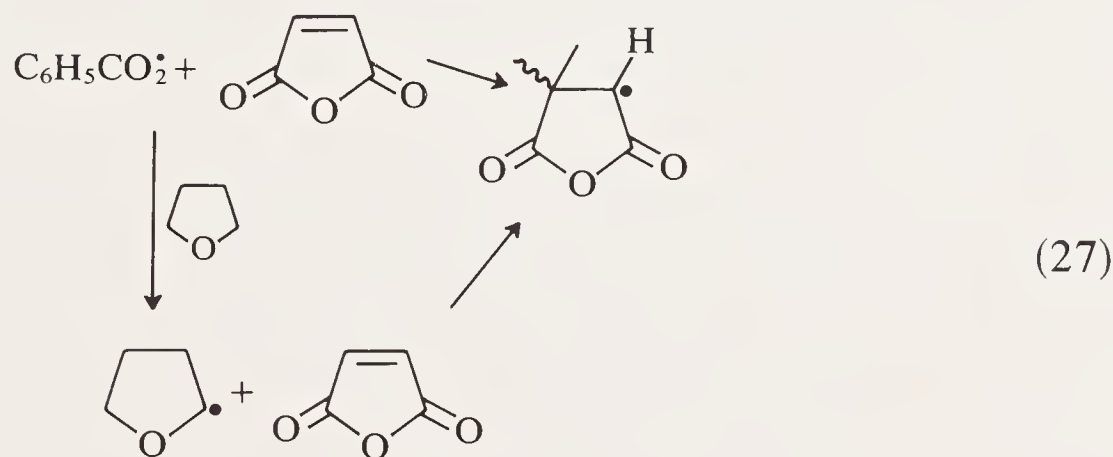
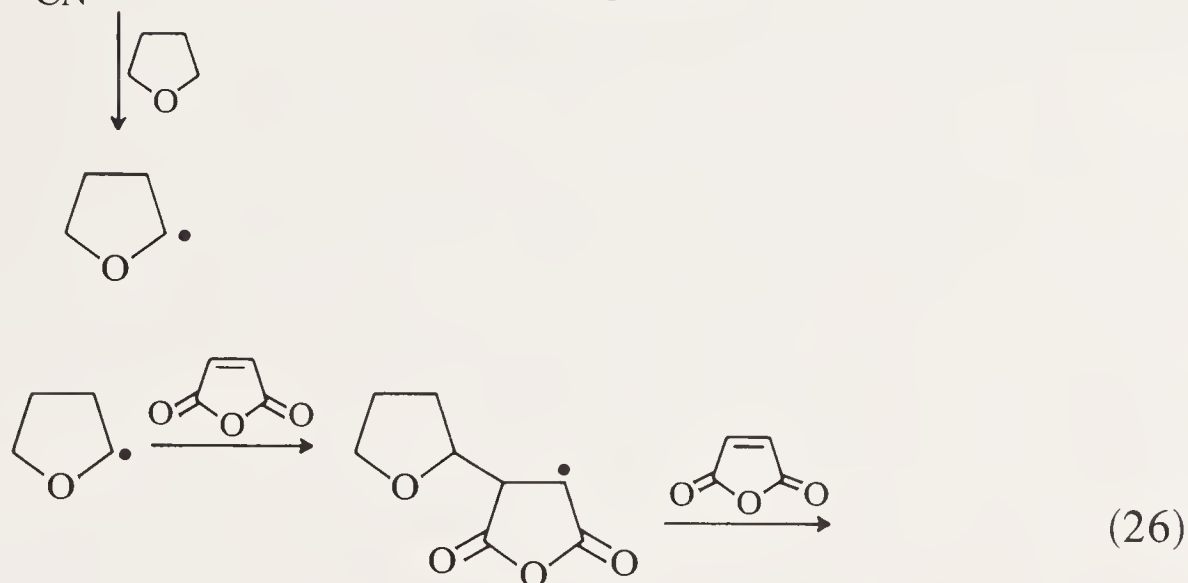
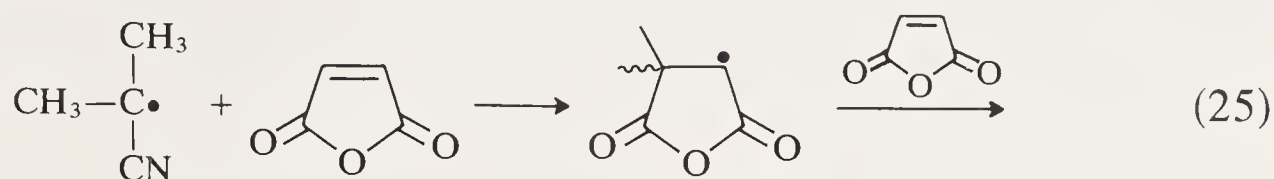
ESR studies<sup>(70)</sup> support the assumption that the conjugated dimeric radical, with the release of secondary hydrogen, can decompose into a conjugated dimer [Eq. (22)]:



Attack of BPO radicals on the rather stable tertiary hydrogen, in contrast to AIBN radicals, might also bring about the following transformations [Eqs. (23) and (24)]:



Addition of small amounts of cyclic ethers, such as THF, brings about enhanced rates of polymerization and yields of polymer for both the AIBN and BPO systems.<sup>(70)</sup> Since THF acts as a very suitable chain-transfer agent, acceleration occurs by the additional route for attacking monomer through the THF radical [Eqs. (25)–(27)]:



The charge-transfer complex formed by MA and the cyclic ether reduces the electropositive charge on the monomer by electron transfer from solvent to monomer. Dioxane, with two oxygens available for complex formation, works best, i.e., gives the highest polymer yields. Free-radical-initiated homopolymerizations may also be accelerated by the use of zinc chloride complexing agent.<sup>(73,74)</sup>

#### 8.2.4. Initiation by Pressure

Maleic anhydride undergoes spontaneous polymerization when heated (100–170°C) under pressure >20,000 atm.<sup>(75,76)</sup> Polymerization was also observed when monomer was subjected to intense transient high pressures and temperatures in shock waves generated by detonation.<sup>(77)</sup> Polymer yields were quite low and remained constant for a wide range of initial temperatures



(25–190°C), dependent on the pressure and compression time.<sup>(78,79)</sup> The polymer with intrinsic viscosity of 0.056 dl/g (2-butanone, 25°C) exhibited a molecular weight of 16,200 (cryoscopy in acetic acid solvent).<sup>(80,81)</sup> The yield of polymer increases with increasing pressure at constant shear stresses and with increasing shear stresses at constant pressure.<sup>(82–84)</sup> In the case of large shear stresses, the polymer becomes partially insoluble, indicating that shear action can produce secondary reactions in the material.

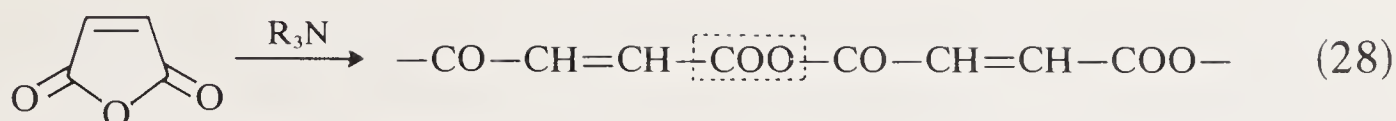
### 8.2.5. Initiation by Ionic Catalysts

Attempts to polymerize MA in chloroform at 20°C with stannic chloride failed.<sup>(48)</sup> Heating the monomer with catalytic amounts of  $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$  at 100°C produced only traces of an undefined product. However, polymer was found in acetic anhydride solvent.<sup>(85)</sup> The catalyst was considered to be a  $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ –acetic anhydride complex. Heating  $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$  in acetic anhydride for 20 h at 100°C, followed by cooling and precipitation with benzene, gave a red powder. This red powder, decomposing to  $\text{SnCl}_4$  at 150–200°C, may be used to initiate homopolymerization of MA.<sup>(85)</sup>

Treatment of MA with *n*-butyl lithium in tetrahydrofuran solvent at 20°C gave an orange-colored product, with IR and NMR showing the presence of double bonds.<sup>(48)</sup> Elemental data supported the assumption that the *n*-butyl lithium had reacted with either the anhydride or carbonyl moiety of the monomer.

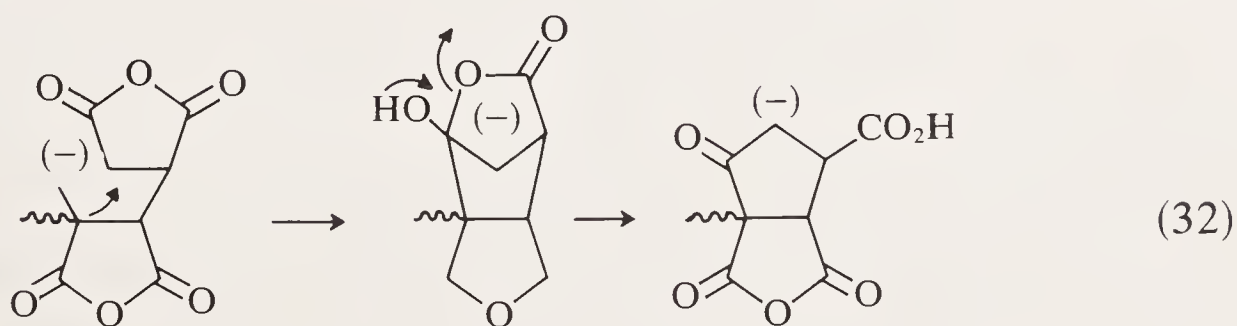
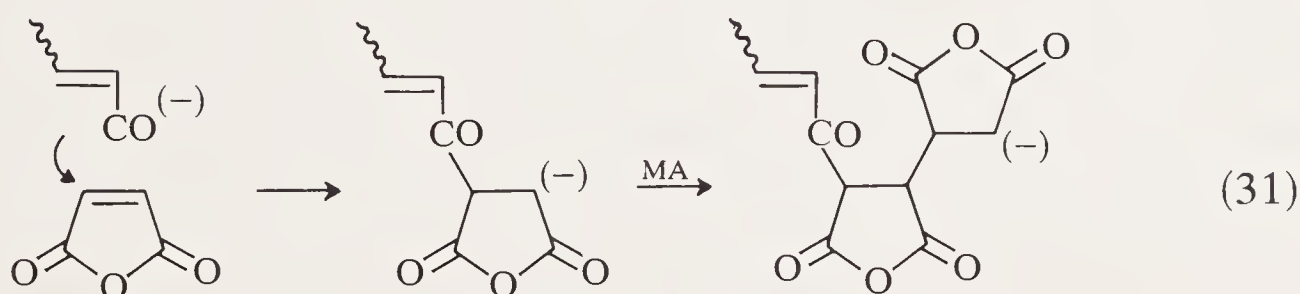
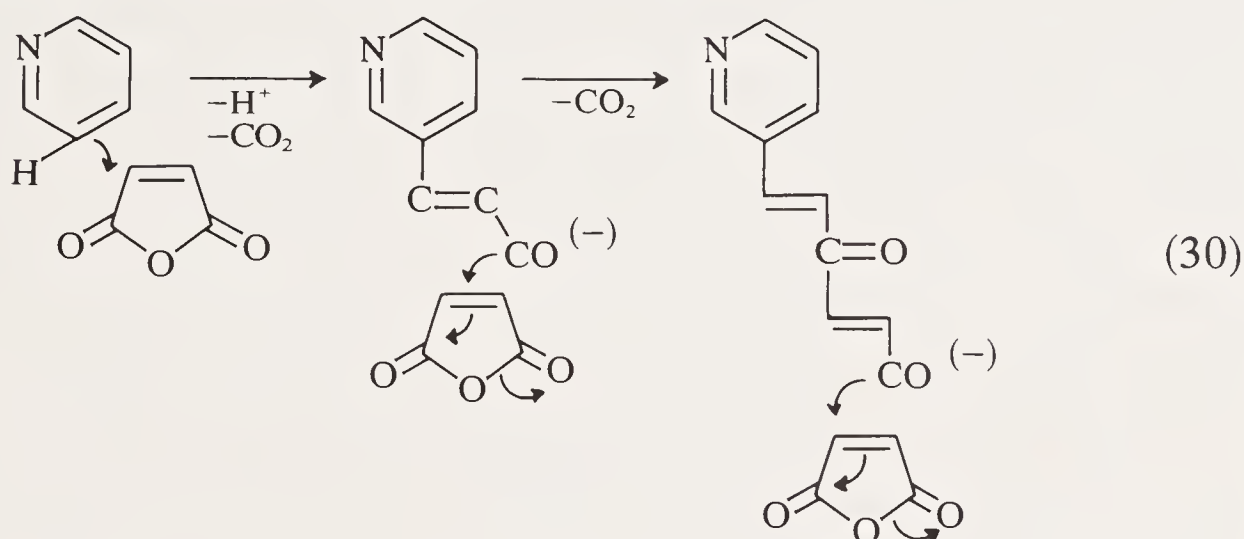
It is well known that a variety of contaminants, such as sodium salts, water, and amines, can drastically decrease the stability of MA at elevated temperatures.<sup>(86,87)</sup> In fact, tertiary amines and MA form explosive mixtures.<sup>(87)</sup> Carbon dioxide is evolved when MA is treated with catalytic amounts of tertiary amines, giving a dark-colored polymeric material soluble in polar solvents.<sup>(86,88)</sup> Homopolymerization of MA, with catalysts such as triethylamine<sup>(86–88)</sup> and pyridine,<sup>(48,89–95)</sup> occurs with decarboxylation and formation of dark-colored products, claimed to be an acrylic acid polymer,<sup>(90)</sup> poly(maleic anhydride),<sup>(91)</sup> or mixtures of the two materials. The polymerizations have been studied in tetrahydrofuran, chloroform, toluene, and pyridine at various temperatures. Reactions with catalytic amounts of pure pyridine proceeded very slowly, with formation of oligomeric and polymeric materials. Small amounts of water, maleic acid, acetic acid, and pyridinium salts aided the polymerization reaction. Radical inhibitors, such as sulfur, 2,2-diphenyl-1-picrylhydrazyl, and anthracene had no influence on reaction rates.<sup>(94)</sup>

Elemental, infrared, and NMR analyses of the materials obtained with tertiary amine catalysts suggested the polymeric structure consisted essentially of *cis*-polyvinylene-ketoanhydride units. Ring opening, followed by decarboxylation, was used to explain the proposed structure **12** [Eqs. (28) and (29)].<sup>(89)</sup>



12

Other units, such as cyclopentanone and succinic anhydride rings, have also been suggested as being present in the polymers obtained with pyridine.<sup>(89,93,95,96)</sup> An anionic polymerization mechanism,<sup>(95)</sup> including initiation by the pyridine-MA CTC<sup>(92,279)</sup> and incorporation of pyridine as a polymer end group, was visualized [Eqs. (30)–(32)]:



As shown, a simultaneous occurrence of two different mechanisms, consisting of 2,5-dioxo-3,4-oxolanediyl and carbonylvinylene residues, was used to account for the proposed polymer structure. In addition, the 2,5-dioxo-3,4-oxolanediyl unit undergoes further rearrangement to give a cyclopentanone moiety.

In light of recent studies by Bacsikai<sup>(67)</sup> and the team of Wurm, Regel, and Hallensleben<sup>(68,69)</sup> on the pyridine-initiated polymerization of MA, the



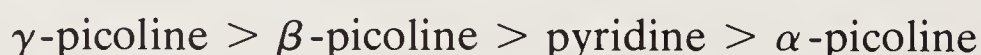
above mechanism, vinylene-ketoanhydride moiety **12** and cyclopentanone structures **10** must be considered as highly improbable. The NMR spectra of the polymers prepared in the Bacskai<sup>(67)</sup> work failed to exhibit olefin and CH<sub>2</sub> resonance peaks. In addition, the H-NMR spectrum of the esterified pyridine-initiated polymer showed no olefin or CH<sub>2</sub> resonance peaks. Furthermore, the methoxy analysis of the esterified polymers indicated that the parent polymers had a substantial number of anhydride rings. These results clearly disagree with the previous proposal that the pyridine-initiated poly(maleic anhydride) contains structures **10**<sup>(89)</sup> and **12**.<sup>(95)</sup> As expected, the methoxy content of the base-initiated polymer was also considerably lower than that required by the conventional theoretical structure, because of decarboxylation.<sup>(67)</sup> In addition, the Wurm *et al.*<sup>(68,69)</sup> work clearly shows that initiation of the pyridine-MA reaction occurs with attack of the pyridine nitrogen toward the MA double bond, giving a betain. Reaction of the ylid derived from the betain, with additional MA, gives a nonlinear 2:1 MA:pyridine reaction product. Some succinic anhydride is also generated in the reaction. These combined efforts show that additional work is in order and must be accomplished before sufficient data are available to convincingly assign a believable structure for the pyridine-initiated polymer.

Electrical conductivity of reaction mixtures and polymerization kinetics have been investigated for the pyridine- and picoline-initiated polymerization of MA.<sup>(96)</sup> In acetic anhydride, it was found that the electrical conductivities of the polymerizing mixtures increased during the course of the reaction. Rates were examined at 25°C and found to increase with both monomer and pyridine concentration. Also, both the conductivity of the reaction mixtures and polymer conversion increased appreciably with increasing temperatures. An apparent overall activation energy was determined to be about 10 kcal/mol and the equation representing the overall rate was formulated as follows:

$$\frac{-d[M]}{dt} = kp[M]^a[I]^b$$

where  $a = 1.3$ ,  $b = 1.2$ ,  $kp$  is the overall rate constant,  $[M]$  the monomer concentration, and  $[I]$  the initiator concentration.

The rates of polymerization and the increase of specific conductivities of the reactivities supported the following order of initiator activity:



Therefore, polymerization rates appear to depend on the basicity of catalysts. The large reduction of polymerization and drop in the specific conductivity of the  $\alpha$ -picoline mixtures is attributed to hindrance of the charge-transfer complex formation by the picoline  $\alpha$ -methyl group.

Maleic anhydride will spontaneously polymerize in the presence of imidazoles, and polymerizations are accompanied by some decarboxylation.<sup>(97)</sup>

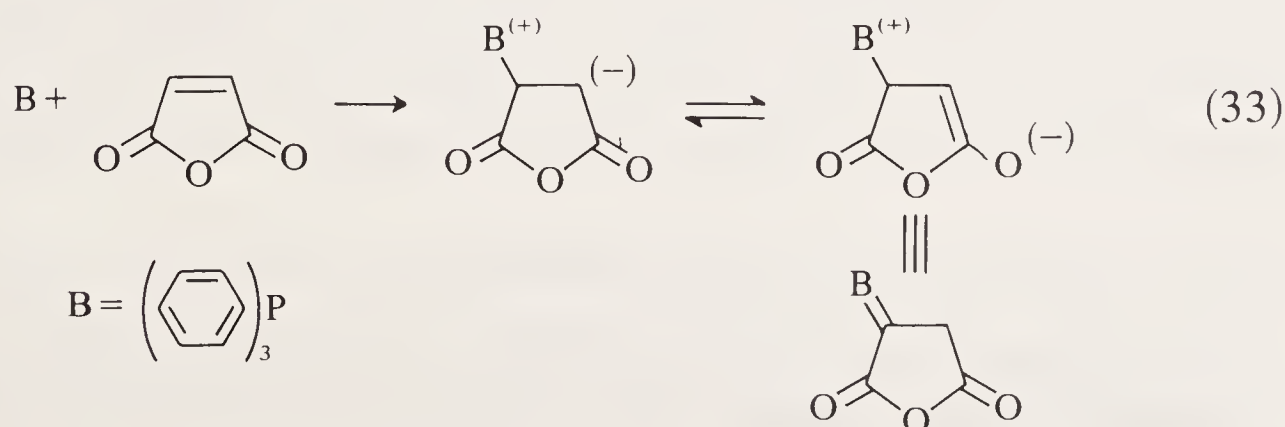


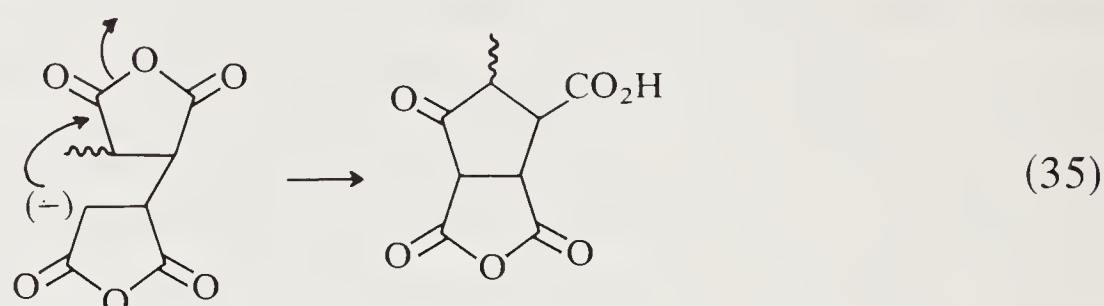
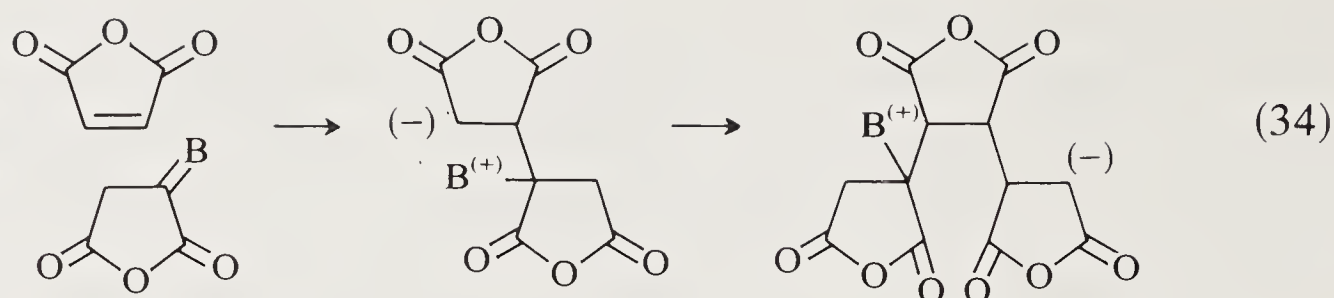
Polymerizations, using a variety of monomeric and polymeric imidazoles, were run both neat and in several solvents at 25–60°C. The polymerizations were claimed to occur through a charge-transfer complex, although the exact role of the CTC in the polymerization mechanism was not clarified. In general, yields, molecular weights, and amount of carbon dioxide generated were maximum when equimolar quantities of reactants were used. When *n*-vinyl-2-methylimidazole was used, the vinyl group did not participate in the polymerization. As expected, polymerizations were not affected by free-radical initiators. These phenomena are similar to those observed earlier when vinylpyridine was used as a catalyst.<sup>(98)</sup> Conversions increased with increasing dielectric constant of the solvent and electroconductivity increased with initiation of polymerizations, giving additional support for an ionic mechanism. The polymers obtained were believed to have 10–12 structural units in the molecular chains. Additional structural units are not precluded.<sup>(97)</sup> The same structural units were proposed in earlier work,<sup>(48,89,93)</sup> with **10** and **12** being improbable according to the Bacsikai<sup>(67)</sup> results. It is interesting to note that MA inhibits the spontaneous polymerization of 2-methyl-5-vinylpyridine.<sup>(99)</sup>

The mechanism of the catalytic action of imidazoles, a spontaneous polymerization, is not totally clarified. Some believe that the imidazole derivative first forms a 1:1 CTC with monomer and then the charge-transfer complexes react with each other.<sup>(97)</sup> This assumption is supported by the experimental observation that the product which is considered to be produced from each reaction is separated by the gel filtration of the reaction mixture.

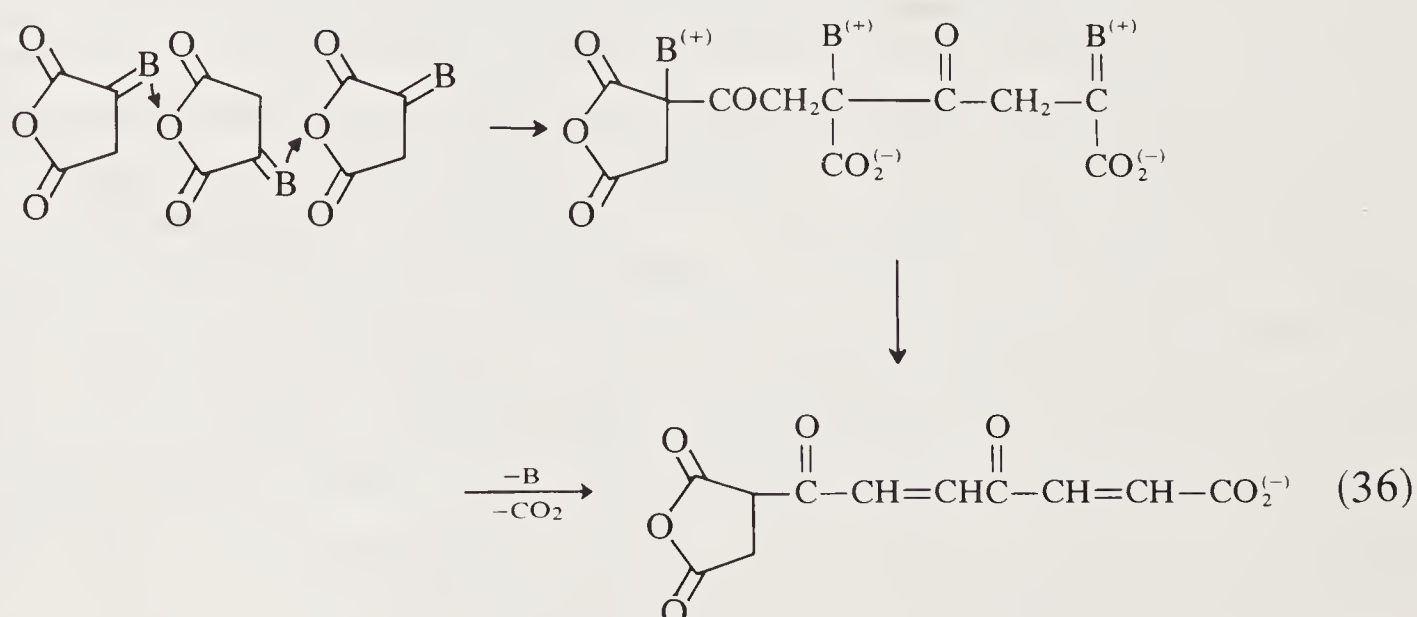
Polymerization, accompanied by carbon dioxide evolution, also occurs when MA is treated with triphenylphosphine or tributylphosphine in benzene, tetrahydrofuran, or dimethylsulfoxide.<sup>(93,100–102)</sup> The polymer, having a molecular weight of 1150, can also be readily prepared with ethyldiphenylphosphine at 100°C in dimethylformamide.<sup>(103)</sup>

The polymer prepared with triphenylphosphine is believed to contain succinic anhydride and cyclopentanone residues formed from further rearrangement.<sup>(100,101)</sup> Polymerizations presumably proceed through an anionic mechanism, involving macrozwitterions. The authors assume that the initiating step is composed of monomer–phosphine reaction to give a ylid and the resulting ylid adds monomer [Eqs. (33)–(35)]:





When tributylphosphine [ $B = (C_4H_9)_3P$ ] is used as an initiator, a conjugated keto-olefinic structure was proposed for the resultant polymer [Eq. (36)]:



Consistent with the proposed structure, the polymer prepared with tributylphosphine exhibited semiconductor properties.

Attempts have been made to polymerize MA with hydridodinitro-gentris-(triphenylphosphine) cobalt,  $CoH(N_2)(PPh_3)_3$ .<sup>(104)</sup> In contrast to acrylonitrile, methyl methacrylate, and other vinyl monomers, which will polymerize with this initiator, no polymer was obtained with MA. In place of polymer, a  $Co(MA)_x(PPh_3)_y$  complex was isolated. Radical anion formation has been observed in the reaction of bis(tricyclohexylphosphine) ethenenickel with MA without polymer formation occurring.<sup>(262)</sup>

#### 8.2.6. Miscellaneous Initiation Methods

Poly(maleic anhydride) is produced in approximately a 70% yield when a mixture of the monomer and a catalytic amount of amorphous nickel



peroxide are heated (90°C) for 69 h.<sup>(105)</sup> The resultant polymer, with m.p. 216–218°C and molecular weight of 1700, exhibits a carbon–hydrogen analysis corresponding to homopolymer.

Both poly(4-vinylpyridine)<sup>(92)</sup> and poly(1-vinyl-2-methylimidazole)<sup>(97)</sup> cause MA to polymerize. In the pyridine case, when a 5% solution of poly(4-vinylpyridine) in chloroform is combined with a dilute solution of MA in chloroform, polymerization proceeds quite rapidly even in air to give poly(maleic acid). Poly(4-vinylpyridine-co-styrene) also initiates polymerization,<sup>(92)</sup> giving a dark-colored material. Polymerizations with 1-vinyl-2-methylimidazole homopolymer and styrene copolymer as initiators were run in dimethylformamide at 25°C and 60°C.<sup>(97)</sup> Molecular-weight studies suggested that two to three monomer molecules were polymerized for each imidazole moiety in the homopolymer and about four anhydride monomer molecules by each imidazole unit in the copolymer. For both homopolymers, polymerization apparently occurred through formation of the charge-transfer complex between monomer–pyridine and monomer–imidazole moieties along the backbone of the polymer molecules. Also, the polymer acted as a matrix for alignment of the monomer molecules.

Maleic anhydride will polymerize electrolytically.<sup>(106,107)</sup> An electric current (0.4–1.8 A) is passed through a cell containing a mercury cathode and a platinum anode in a porous porcelain cup containing a dimethylformamide solution of tetraethylammonium-*p*-toluenesulfonate. The cup is immersed in a catholyte solution comprising MA quaternary ammonium salt and dimethylformamide. Using a cell voltage of 13–24 V and a cathode potential of –2 V versus an Ag–AgCl reference electrode, polymerizations were run at 35–65°C. A quantitative yield of polymer, having a molecular weight of 2600, was obtained after 3.5 h. Acetic anhydride is also useful as a solvent, but dimethylformamide gives the best yields. The yield of polymer increased with increasing quantity of electricity passed through the solution with time; however, the molecular weight was nearly independent of the quantity of electricity. The infrared spectra of the polymers were similar to those prepared using pyridine as an initiator.

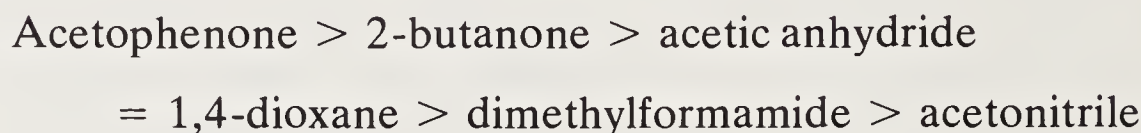
A patent disclosure claims the polymerization of polar vinyl monomers in a constant electric field.<sup>(108)</sup> No details were available to the authors on this method of polymerizing MA.

### 8.3. PROPERTIES

Poly(maleic anhydride), prepared with free-radical initiators, is a low molecular weight, creamy white material soluble in water, dilute alkali, ketones, acetonitrile, lower alkyl alcohols, esters, and nitroalkanes. Nonsolvents include aromatic hydrocarbons and most chlorinated compounds. The



following order<sup>(22)</sup> of solvent power was established by measuring intrinsic viscosities of a polymer having a light-scattering molecular weight of 23 100:

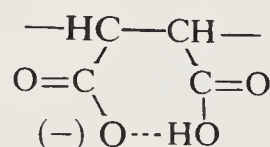


The infrared spectrum of the polymer, analogous to the monomer, exhibits strong carbonyl peaks at approximately 1859 and 1880  $\text{cm}^{-1}$ . The main difference is that the peaks are much broader in the polymer spectrum.<sup>(39,56)</sup>

The NMR spectrum (DMSO- $d_6$ ) exhibits a broad resonance at  $5.9\tau$  for the CH residue and a resonance at  $3.7\tau$  in the case where the polymer also contains carboxylic acid moieties.<sup>(107,109)</sup> Pyrofield ion mass spectrometry (PFIMS), gas chromatography (GC), and infrared spectroscopy have been used to study the degradation behavior of poly(maleic anhydride),<sup>(66,110)</sup> which decomposes at its m.p. 320°C.<sup>(22)</sup> At 540°C, the strongest peak on the gas chromatography chart was produced by water: the polyanhydride readily reacts with water vapor to form carboxyl groups. On heating, the acid form of the polymer easily splits out water and returns to the anhydride form. Various reaction paths and mechanisms have been proposed to account for the most prominent (primary) masses in the PFIMS of the polymer.<sup>(110)</sup>

Poly(maleic acid) is readily obtained by hydrolysis of the parent polymer. This acid polymer is a polyelectrolyte with a high potential charge on every carbon atom on the polymer backbone. Thus, the polyelectrolyte properties of this polymer differ from poly(acrylic acid) or poly(methacrylic acid). Titration of poly(maleic anhydride) with LiOH, NaOH, KOH, and  $(\text{CH}_3)_4\text{NOH}$  results in titration of half of the actual carboxyl groups; i.e., the titration curve shows only one inflection at the half-neutralization point.<sup>(10,111)</sup> Thus, the polymer normally behaves as a monobasic polyacid in potentiometric titration. A discussion of MA titration is provided in Sec. 3.4.1.

The concept has been offered<sup>(112)</sup> that the mono ion of the maleic acid unit, from the first dissociation step of the homopolymer, has a stable ring structure **13** resulting from intramolecular hydrogen bonding.



**13**

During subsequent neutralization, the increasing charge of the polyion and the adjacent ionized groups substantially reduce the second ionization constant, resulting in the absence of the second potential drop in the titration curve. When a supporting electrolyte, providing an ion common to that of

the base, is added in sufficient concentration during titration, the polymer titrates as a dibasic polyacid with two inflections on the potentiometric titration curve.<sup>(22,113)</sup> The common ion suppresses the ionization of the first carboxyl groups titrated and strongly diminishes the neighboring group interactions.

When divalent metal hydroxides, such as  $\text{Ba}(\text{OH})_2$  are used, the carboxyl groups in poly(maleic acid) are titrated without differentiation; i.e., there is only one inflection point in the titration curve at full neutralization.<sup>(22,112)</sup>

Monovalent counterions have great influence on the ionization of poly(maleic acid). In the first dissociation step the pH values, at a given degree of neutralization, decrease in the order  $(\text{CH}_3)_4\text{N}^+ > \text{Li}^+ > \text{Na}^+ > \text{K}^+$ . In the second dissociation step the pH values decrease in the order  $(\text{CH}_3)_4\text{N}^+ > \text{K}^+ > \text{Na}^+ > \text{Li}^+$ , analogous to the behavior of ordinary polycarboxylic acids. The binding strength of the alkali-metal ions to the primary carboxylate groups is in the order  $\text{K}^+ > \text{Na}^+ > \text{Li}^+$ , indicating that the strength of the ion pairs increase with the decrease in the radius of the hydrated alkali-metal ion. For the secondary carboxylate groups, the binding order of  $\text{Li}^+ > \text{Na}^+ > \text{K}^+$  is related to the ionic radius of the alkali metal, i.e., the smallest ion is bound to the largest extent.<sup>(112)</sup> It is believed that in the first neutralization binding involves hydrated alkali-metal ions, while in the second dissociation step substantially bare alkali-metal ions participate in binding with the secondary carboxylate groups.

Dilatometry studies indicate that distinctly larger volume increases accompany the protonation of half-neutralized poly(maleic acid) when  $(\text{CH}_3)_4\text{N}^+$  ions are the counterions, but not when the ions are either  $\text{Li}^+$  or  $\text{Na}^+$ . This is consistent with the finding already derived by different experimental means that  $\text{Li}^+$  and  $\text{Na}^+$  are extensively site bound while  $(\text{CH}_3)_3\text{N}^+$  ions are only "loosely" bound to the poly(maleic acid) macroions.<sup>(114)</sup>

The relative<sup>(22)</sup> and reduced<sup>(115)</sup> viscosities of aqueous solutions of poly(maleic acid) neutralized with NaOH increase as the degree of neutralization is increased, reaching a peak at the half-neutralization point, and then decrease.

When heated with polyethylene, in the presence of radical initiators, poly(maleic anhydride) becomes grafted to the polyolefin,<sup>(116,117)</sup> with a grafting degree of 4.4% (see Sec. 11.1). The properties of this type material are more appropriately discussed in Chapter 11.

## 8.4. MA POLYMER USES

A large number of possible uses exist for poly(maleic anhydride), poly(maleic acid), and derivatives of these two polymers. Some of these uses, described or claimed in patents and/or other publications, include prevention



of scale or deposits in areas where the water has high  $\text{CaCO}_3$  content,<sup>(118-120)</sup> removal or prevention of boiler scale,<sup>(120,121)</sup> prevention of scale formation in heat exchangers,<sup>(122)</sup> scale reducer for sea water evaporators,<sup>(123,252)</sup> water purification agents,<sup>(124)</sup> metal coatings to prevent corrosion,<sup>(125,126,252,266)</sup> and coatings for steel ingot casting moulds.<sup>(280)</sup> A recent patent<sup>(249)</sup> claims that very small amounts of maleic acid telomers are very useful for the crystallization of anhydrous sodium carbonate from saturated sodium carbonate solutions. The telomer additive reduces the transition temperature of the monohydrate to anhydrous sodium carbonate, bringing about rapid crystallization at 104–109°C. The resins have potential utility as sizing for fibers,<sup>(126-130)</sup> antistatic additives for plastics and fibers,<sup>(131-133)</sup> detergent builders,<sup>(134-139,252-254)</sup> mechanical cleaner additives,<sup>(140-142)</sup> pigment dispersing agents,<sup>(143,144)</sup> and leveling agents for dye baths. In the areas of inks<sup>(145)</sup> and adhesives,<sup>(146,147)</sup> a small amount of the polymer in formulations may give improved properties. Crosslinked polymers could have use in ion exchange resins.<sup>(148)</sup> The resin can be used to cure epoxy resins,<sup>(149-152,171)</sup> crosslink keratin materials,<sup>(153-155)</sup> act as a reagent to immobilize enzymes,<sup>(139,156)</sup> bind oxidation–reduction moieties<sup>(157)</sup> and  $\text{Ca}^{2+}$  ions,<sup>(158)</sup> and perform as a dye-assist agent.<sup>(159,168)</sup> Possible use of the polymer has also been explored in nitration,<sup>(160)</sup> cationic polymerization,<sup>(161)</sup> matrix polymerization systems,<sup>(162-164)</sup> and lithographic printing applications.<sup>(165)</sup> The polymer and derivatives of the material have been examined in animal feeds.<sup>(166)</sup> Tin derivatives of the polymer have potential use in bactericidal and virucidal applications.<sup>(167)</sup> Uses have also been claimed for the amine and phosphine prepared materials.<sup>(167,169)</sup>

Possibly the greatest potential use for poly(maleic anhydride) exists in the detergent, scale prevention, etc., water treatment areas. In fact, the increasing demand for pollution control and replacement of phosphates for detergents could open up a sizable market for poly(maleic anhydride) or MA copolymers and their hydrolyzed products.<sup>(260)</sup> Methods are available to prepare decolorized polymers for detergent formulations.<sup>(170)</sup>

Under several patents,<sup>(172-178)</sup> Ciba–Geigy Corporation markets poly(maleic anhydride) or poly(maleic acid) materials known as Belgard EV, Belclene<sup>TM</sup> 200, and Belclene<sup>TM</sup> 523.<sup>(179)</sup> Belgard EV is a liquid treatment for controlling scale deposition in sea water distillation plants. Belclene<sup>TM</sup> 200, which comes in either a solid or liquid form of the acid, is used for scale control in boilers and cooling water systems. Belclene<sup>TM</sup> 523, which is composed of the low-molecular-weight polymeric carboxylic acid, a zinc salt, and benzotriazole in water, is employed as a corrosion inhibitor. The Ciba–Geigy Corporation has recently filed a petition with the Food and Drug Administration proposing the food additive regulations be amended to provide for the use of hydrolyzed poly(maleic anhydride) and its sodium salt or boiler water additives in the preparation of steam that will contact food.<sup>(261)</sup>



## 8.5. MA-BASED MONOMERS

### 8.5.1. Substituted MA

Little has been published on techniques for achieving the homopolymerization of mono or disubstituted MA monomers (see Chapter 3). Thamm and Hensinger<sup>(183)</sup> recently showed that  $\gamma$  irradiation of dichloromaleic anhydride (DCMA) in benzene produced a polymer as the main product. The yield and molecular weight of the polymer increased with radiation dose. The polymer backbone contained chlorophenylsuccinic anhydride residues. It was shown that chlorophenylmaleic anhydride was produced during the reaction. Under the same conditions, dimethylmaleic anhydride (DMMA) failed to polymerize with free-radical, ionic, and UV initiation with sensitizers.<sup>(82,83)</sup> Presumably, techniques may be found for the homopolymerization of chloro or phenylmaleic anhydride. Chloromaleic anhydride (CMA) reacts with methyl radicals more readily than MA and much more readily than DCMA.<sup>(184)</sup> This, coupled with halogen activation and ring coplanarity, should allow CMA to be homopolymerized. It is known that CMA will copolymerize with styrene, methyl methacrylate, butadiene, cyanoacrylates, and other olefins.

### 8.5.2. Maleic and Fumaric Acids

Very little has been published on the homopolymerization of maleic or fumaric acid. Sato and coworkers<sup>(180)</sup> recently reported that maleic acid was easily polymerized with  $K_2S_2O_8$  in water in the presence of poly(*N*-vinylpyrrolidone), to form approximately a 1:1 polymer complex. The formation of the complex was accelerated by increasing temperature, concentration of initiator and acid, and molecular weight of the poly(*N*-vinylpyrrolidone). The poly(maleic acid) portion of the complex decomposed at 100–130°C. The complex forms by hydrogen bonding. Both maleic and fumaric acid are reported to undergo oligomerization when subjected to high pressure and shear stress, to give products with molecular weights of 600–800. Oligomerization is believed to occur by ionic addition of the carboxyl group of one molecule to the double bond of another.<sup>(181)</sup> It is also known that maleic and fumaric acids may be treated with phosgene and trialkylamines to give *cis*- and *trans*-poly(vinylketoneanhydrides).<sup>(182)</sup> Both these polymerizations occur by a condensation or step-growth mechanism. There appears to be no published report on the addition homopolymerization of fumaric acid. However, the two acids are known to copolymerize with other vinyl monomers, using free-radical initiators.<sup>(58)</sup>

### 8.5.3. Maleate and Fumarate Half-Esters

Maleic anhydride reacts with alcohols to give alkyl hydrogen maleates (see Chapter 3). Isomerization gives alkyl hydrogen fumarates. These

monomers are resistant to homopolymerization. However, the UV-initiated polymerization of cadmium octadecyl fumarate in multilayers or thin films has been reported.<sup>(185)</sup> Allyl hydrogen maleate (see Chapter 10)<sup>(186)</sup> and diallyl maleate or diallyl fumarates<sup>(196,247)</sup> polymerize with free-radical initiators to give a polymer with lactone rings, which is appropriately considered a cyclo-copolymerization reaction. The polymerization of the allyl maleate is highly enhanced by morpholine, due to isomerization.<sup>(281)</sup> The alkyl hydrogen maleates and fumarates copolymerize with other vinyl monomers,<sup>(58)</sup> with the fumarates being most reactive. A kinetic study<sup>(184)</sup> of the addition of methyl radicals to these esters indicates that the transition state involving maleates is less resonance stabilized due to noncoplanarity of the carboxyl groups. Maleic anhydride, however, is planar and even more reactive than fumarate esters. In recent years, interest in these monomers has centered about using the materials as copolymerizable surfactants.<sup>(187-194)</sup> Butyl and octyl hydrogen maleate are produced for internal usage by several large manufacturers of emulsion polymers as polymerizable emulsifiers.

#### 8.5.4. Dialkyl Maleates and Fumarates

Diester derivatives of maleic and fumaric acid (see Chapter 3) are not easily polymerized. However, they do yield soft, tacky thermoplastics with free-radical generating initiators such as BPO. Diethyl fumarate, for example, polymerizes to an 89% yield of poly(ethyl succinate) when heated in the presence of 2% BPO for 7 h.<sup>(195)</sup> Liquid-phase (neat) reaction at high pressure (5000 psi) improves the yield.<sup>(45)</sup> Polymers of higher softening point and higher molecular weight may be prepared by emulsion-polymerization techniques.<sup>(197)</sup>

The fumarates polymerize much more readily than the maleates, since the transition state involving maleates is less resonance stabilized due to noncoplanarity of the carboxyl groups.<sup>(184)</sup> Derivatives of dialkyl maleates and fumarates have also received attention as copolymerizable surfactants.<sup>(198-201,238,250)</sup> Significant attention has been given to the polymerization properties of alkyl allyl maleates,<sup>(204-207)</sup> diallyl maleates, and fumarates<sup>(107,263,264,275)</sup> and propargyl esters of the two acids.<sup>(208)</sup> Free-radical-initiated polymerization, both in bulk and solution, produces polymers with a high percent of cyclic structures. Copolymerization with other vinyl monomers, such as styrene, significantly reduces lactone formation.<sup>(225)</sup>

Information on maleate and fumarate ester copolymerizations may be found in Chapters 9 and 10 and various review articles.<sup>(58,202,203,209)</sup> The glass transition temperatures ( $T_g$ ) for a series of dialkyl fumarates has recently become available,<sup>(265)</sup> facilitating the design of polymers containing these monomers. Dibutyl and dioctyl maleates and fumarates are fairly large-volume chemicals, employed as plasticizing comonomers for vinyl acetate emulsion



coatings. Recent patents<sup>(255)</sup> disclose that dialkyl maleates or fumarate terpolymers made with methacrylic acid and diolefins are also excellent thickeners for emulsion coatings. Dimethyl maleate is being used to some small extent as a hardening comonomer for vinyl acetate copolymer films and was recently claimed<sup>(259)</sup> useful for preparing antifouling coating compositions.

Diglycidyl maleate and fumarate are potentially two very attractive monomers that have received very little study.<sup>(258)</sup> Providing they have no adverse physiological or toxicological properties, they could become very useful for preparing a wide variety of new epoxy-containing polymers and also function as epoxy resin reactive diluents. The reduced volatility, and greater epoxide oxygen content of these monomers, compared to glycidyl acrylate or methacrylate, supports this thought.

#### 8.5.5. Maleamic and Fumaranilic Acids

Maleic anhydride may be treated with primary or secondary amines to obtain maleamic or fumaranilic acids (see Chapter 3). Treating MA with urea gives the monoureide. These monomers, which are also resistant to homopolymerization, have had only meager copolymerization study. Copolymerization of the methyl ester of *N*-carbamoyl maleamic acid with styrene progresses readily in dioxane or acetone at 70°C, with typical free-radical initiators.<sup>(237)</sup> Hydrolysis produces a copolymer with maleamic acid residues. Thermolysis produces a copolymer with imide moieties. The little explored monoureide, as a tri functional monomer, is potentially exploitable in the production of a large variety of thermosetting copolymers<sup>(235)</sup> and polyelectrolytes derived from acrylic or methacrylic acid copolymers.<sup>(242)</sup> Copolymers prepared from maleamic acid with anthraquinone residues are potentially useful water-soluble polymeric dyes.<sup>(245)</sup> Copolymers of *N*-stearylmaaleamic acid and acrylic esters were recently claimed to be useful as release backings for adhesive tapes.<sup>(256)</sup>

#### 8.5.6. Maleimides

Unlike MA, maleimide (MI) (see Chapter 3) homopolymerization is very facile. Using organic peroxides and AIBN initiators, poly(succinimide) is obtained with molecular weights as high as  $10^6$  and softening point  $>400^\circ\text{C}$ .<sup>(210,211,221)</sup> Maleimide is also readily polymerized with  $\gamma$  ( $^{60}\text{Co}$ )<sup>(212,213,217,244)</sup> and UV radiation<sup>(214,239)</sup> and electrochemically.<sup>(251)</sup> MI and MA, which form a eutectic mixture at 26 mol % MI, copolymerize with  $\gamma$ , UV, and free-radical initiation.<sup>(244)</sup> The amorphous copolymer, produced in dioxane at 70°C, with AIBN, is rich in MI. The rate of MI homopolymerization is increased with addition of complex-forming zinc chloride to the



systems.<sup>(73,74)</sup> Nakayama and Smets<sup>(230)</sup> obtained a rather unusual rate expression for MI polymerization.

$$R_p = k[\text{MI}]^{1.1-1.3}[\text{Initiator}]^{0.8}$$

The intramolecular formation of a stabilized radical on the succinimide residue was postulated to explain the 0.8 order in the initiator. The activation energy for MI polymerization is 21.0 kcal/mol, compared to 14.0 kcal/mol for MA polymerization.<sup>(248)</sup> The enthalpy difference, attributed to the enhanced strain in MI, accounts for the remarkable polymerizability of MI.

Anionic polymerization of MI is also known.<sup>(215,227)</sup> Hydrogen migration occurs during polymerization with strong bases.<sup>(230,241)</sup> The polymer apparently consists of 75–85% rearranged structure and 15–25% conventional ones. The rate was zero order in the monomer, explained by assuming a rapid complex formation between the propagating specie and the monomer followed by a slow rearrangement of the complex to a new propagating anion. Consequently, it is postulated that the rate-determining step is an intramolecular rearrangement reaction. Succinimide suppresses the rate of anionic polymerization.

A large number of *N*-substituted maleimides have been prepared and shown to homo and copolymerize readily with other vinyl monomers, using free-radical,  $\gamma$ , and UV radiation.<sup>(58,73,74,213,214,216-220,222-228,232-234,240,267-269)</sup>

There is much activity in the area of maleimide polymerizations. For example, a recent patent<sup>(243)</sup> describes synthesis and polymerization of maleimides to prepare polymeric antioxidants. Minoura<sup>(229)</sup> reviewed MI copolymerizations.

Bismaleimides, prepared from diamines and MA (see Chapter 12), have also been copolymerized with indene, *N*-vinyl-2-pyrrolidinone, acrylamide, divinylbenzene, and mixtures of vinyl monomers to prepare new crosslinked molded materials.<sup>(271,272,274)</sup> For example, a 50.0:15.5:29.2 parts by weight mixture of bis(4-maleimidophenyl) methane: *N*-vinyl-2-pyrrolidinone: styrene, containing 0.049% tetrachloro-1,4-benzoquinone was polymerized at 125°C for several minutes to a resin with 1 P viscosity. Hardening the resin for 2 h at 120°C and 24 h at 150°C gave a translucent molding with flexural strength 16.9 kg/cm<sup>2</sup> and flexural modulus 190 kg/cm<sup>2</sup>.<sup>(272)</sup>

Bismaleimides undergo successive 2 + 2 and 2 + 4 cycloaddition reactions with benzene and alkyl-substituted benzenes on exposure to ultraviolet light.<sup>(273)</sup> In the case of unsymmetrical bismaleimides or substituted benzenes, head-to-head, head-to-tail, and tail-to-tail polyimide structures are obtained. These polyimides are stable to >400°C.

Isomaleimides, analogous to MA, do not undergo facile polymerization.<sup>(231)</sup> Free-radical bulk and solution polymerization of *N*-alkyl and aryl isomaleimides proceeds slowly to give low-molecular-weight polymers.<sup>(277)</sup> Analogous to MA and MI, isomaleimides tend to undergo free-radical-

initiated equimolar copolymerization with many electron-donor monomers. Isomaleimides are known to perform as fungicides and defoliating agents.<sup>(270)</sup>

Of all the MA-based monomers the maleimides and bismaleimides (see Chapter 12) would appear to offer the greatest potential for future commercial exploitation. The maleimide residue helps to improve the heat and chemical resistance, as well as raise the glass transition temperature, of polymeric materials.<sup>(228)</sup> Bismaleimides are also known to improve the adhesion of rubber to textile fibers, giving improved vulcanizates.<sup>(282)</sup> The *N*-phenyl-maleimide copolymers would appear to hold particular promise as new materials.<sup>(246)</sup>

#### 8.5.7. Maleonitrile and Fumaronitrile

Homo and copolymerization of maleonitrile and fumaronitrile have been achieved by using medium-high temperature free-radical initiators, such as di-*tert*-butyl peroxide.<sup>(236)</sup> Copolymerization of the two monomers, with other vinyl monomers, particularly electron-donor monomers, is readily achieved with typical free-radical initiators.<sup>(58)</sup> Black, non fusible but soluble homopolymers are obtained. Spectroscopic and chemical evidence shows that polymerization occurs through the nitrile moieties to give polymers with 1-pyrroline rings.<sup>(236)</sup>





# RANDOM ADDITION COPOLYMERIZATIONS

## 9.1. INTRODUCTION

It was explained in Chapter 8 that MA is not easily homopolymerized. However, it is known that this monomer will readily copolymerize with a great variety of other monomers. In fact, many 1,2-substituted monomers, which will not normally undergo free-radical polymerization due to kinetic effects, will yield copolymers with MA present. This being true, MA copolymerizations continue to be studied, for a better mechanistic understanding of why and how these copolymerizations occur. Also, MA copolymerizations are being explored as a technique to improve the physicochemical properties of polymers by providing increased polarity, rigidity, glass transition temperature, and functionality. The MA residue on the polymer backbone is known to promote hydrophilicity and adhesion, improve dyeability and heat distortion, give functionality for crosslinking and other chemical modifications, as well as promote compatibility with other polymers and fillers. It will be seen in both this chapter and Chapter 10, how these physical and chemical attributes have been exploited to make many copolymers, useful or potentially useful in the coatings, adhesives, plastics, and fiber industries.

A great amount of work has been reported on the determination of the copolymerization parameters for a large number of monomer pairs,<sup>(1-4)</sup> since the Alfrey, Bohrer, and Mark<sup>(5)</sup> book in 1952 entitled *Copolymerization* and Flory's<sup>(6)</sup> classical text in 1953, *Principles of Polymer Chemistry*. This additional work was stimulated by the knowledge that the magnitude of the copolymerization parameters, i.e., reactivity ratio  $r_1$  and  $r_2$  values, are useful for calculating copolymer composition as a function of conversion, determining monomer sequence along polymer chains, and establishing programmed addition ratios of reactive monomers to obtain desired copolymer formulations. Also, the calculated compositions may be used to predict properties and performances of copolymers and assist in the selection of optimum process conditions for a desirable material. This being true, the  $r_1$  and  $r_2$  values of MA and comonomers, for which the reactivity ratios have been estimated, have been collected from the literature and listed in the table in the appendix to this chapter. The information is viewed as important to those involved in the synthesis and manufacture of MA copolymers. For those wishing further

explanation of the copolymerization parameters, an addendum on this subject follows the table in the appendix to this chapter.

In this chapter we review and discuss random (nonequimolar) MA copolymerizations, covered by the condition  $r_1 r_2 \approx 1$ , and provide a comprehensive patent coverage on uses for these materials. Some attention is also given to discussing copolymerizations of MA-based monomers, such as maleates and fumarates, since over the years substantial study has been devoted to trying to find uses for these monomers and polymers. Chapter 10 covers the very frequent conditions for MA copolymerizations where  $r_1 r_2 \approx 0$ .

## 9.2. COPOLYMERIZATIONS, MONOMERS STUDIES

### 9.2.1. Styrene Monomers

Styrene,  $\alpha$ -methylstyrene, vinyl toluene, etc., monomers undergo both equimolar (see Chapter 10) and nonequimolar, free-radical-initiated copolymerization with MA, depending on monomer feed ratios and polymerization conditions.<sup>(30,109–121)</sup> The ratio of reactants may be varied over a wide range, but it can be shown by chemical analysis that styrene and MA are present in the copolymer in a 1:1 ratio when MA is present at the start of the reaction in equal or excess molar ratio. The tendency to give a 1:1 copolymer holds down to low concentrations of MA in the monomer feed mixtures. From the published reactivity ratios (see table in appendix to this chapter), it is evident that the maleic free radical on the end of a growing polymer chain never reacts with MA monomer, and a chain ending in styrene radical will seldom react with styrene monomer unless a very high concentration of free styrene is present.<sup>(122)</sup> Thus, to prepare a homogeneous copolymer with only 5–10 mol % MA, copolymerizations must be run with an extremely low concentration of MA present during the entire reaction course. Cationic initiators have also been explored for preparing styrene–MA copolymers,<sup>(124)</sup> but little information is available on such materials.

Polymerization of the styrene–MA monomer pair is highly exothermic, unless controlled by initiator selection, cooling, or use of diluents. The reaction is often run in solution with peroxide initiators at temperatures of 50–150°C. Where the difference in the solubility parameter of the solvent and the copolymer exceeds 1.4 Hildebrand heterogeneous-phase copolymerization is observed, otherwise a homogeneous-phase polymerization occurs.<sup>(30)</sup> The rates of polymerization are greatest under heterogeneous phase conditions. Addition of MA to a polymerizing solution of styrene is one procedure frequently employed to make a copolymer with <50 mol % anhydride.<sup>(121)</sup> Continuous bulk polymerization techniques have also been recently developed for producing nonequimolar, homogeneous styrene–MA copolymers.<sup>(547)</sup>



Copolymers with excess styrene are also conveniently prepared in high conversion by incremental addition of monomers and initiator mixtures to refluxing *p*-cymene.<sup>(117)</sup> Various other techniques have also been described for preparing random styrene-MA copolymers,<sup>(125-132)</sup> including UV-initiated copolymerization,<sup>(133)</sup> but not all methods produce homogeneous copolymers having a narrow composition distribution. One technique employed consists of copolymerizing monoalkyl maleates and styrene in excess alcohol with peroxide initiators.<sup>(134,495)</sup> Under comparable conditions, fumarates copolymerize much more readily with styrene than maleates.<sup>(1)</sup> Hydrolysis and heating converts these esters to styrene-MA copolymers.<sup>(135)</sup> The maleate copolymers may also be prepared by a suspension process with poly(vinyl alcohol) as a dispersant and benzoyl peroxide (BPO) initiator. Hydrolysis and drying provides the copolymers with low anhydride content (3-5%).<sup>(136)</sup> The effects of electron-donor solvents on styrene copolymerization with maleic acid, monodecyl maleate, and monooctyl maleate have been studied, with reactivity ratios tabulated.<sup>(137)</sup> The nature of the solvent significantly affected the reactivities of the monomers. The effect of the penultimate monomer unit on the polymer chain was particularly strong in weak electron-donor solvents; whereas it was substantially decreased or nonexistent in strong electron-donor solvents.

The styrene-MA copolymer gross inhomogeneity may be detected by cloudiness or haze in a cast or pressed film. Solubility tests may also be used to reveal poor composition homogeneity. However, fractionation, gel permeation chromatography, light scattering, and ultracentrifugation are the best techniques to ascertain copolymer homogeneity.<sup>(138)</sup> These analytical techniques are viewed important when trying to select a procedure for preparing random styrene-MA copolymers, with excess styrene monomer within the copolymer chains.

Solubility characteristics and solubility parameters ( $\delta$ ) have been determined for styrene-MA copolymers of different molar compositions (Table 9.1).<sup>(113,118,138)</sup> Good solvents for styrene-MA copolymers include ethyl acetate, butyl acetate, 2-butanone, 4-methyl-2-pentanone, dioxane, tetrahydrofuran, and *N,N*-dimethylformamide. Schneier<sup>(118)</sup> developed an equation for calculating the  $\delta$  values of random styrene-MA copolymers, having the following form:

$$\delta_x = \frac{(n_1 M_1^2 / p_1) \delta_1 + (n_2 M_2^2 / p_2) \delta_2}{(n_1 M_1 + n_2 M_2) [(n_1 M_1^2 / p_1) + (n_2 M_2^2 / p_2)] (1/P_x)^{1/2}}$$

Where  $n$ ,  $M$ ,  $p$ , and  $\delta$  refer, respectively, to the number of moles, monomer molecular weight, polymer density, and solubility parameters, and the subscripts 1, 2, and  $x$  refer, in turn, to components 1, 2, and mixture.

The Schneier<sup>(118)</sup> equation permits calculation of the solubility parameter of a mixture from data available on the pure components. Conversely, if the



Table 9.1 Physical Properties of Styrene-co-MA Polymers<sup>a</sup>

Physical property evaluated <sup>b</sup>	(mol %)				
	0	5	18	25	33
$M_{\eta} \times 10^{-3}$ (Osmometry)	87.5	82	75.4	79.6	75.2
$M_{\eta} \times 10^3$ (GPC)	90.4	82	84.0	79.6	65.1
$M_w \times 10^3$ (GPC)	195.1	175.2	184.3	177.6	146.4
$M_w/M_{\eta}$ (GPC)	2.16	2.14	2.20	2.26	2.25
$\eta$ (10% in 2-butanone)	4.06	3.92	4.07	3.96	4.19
Solubility parameter $\delta$	9.18	9.314	9.729	9.874	9.907
Glass transition temperature ( $T_g$ ), °C	—	106	—	—	155
DTA Maximum <sup>b</sup> endotherm, <sup>c</sup> °C	95	111	131	133	153

<sup>a</sup> From Reference 138.  
<sup>b</sup> Combinations of tetrahydrofuran (THF)/H<sub>2</sub>O, THF/ $\alpha$ -pinene and acetone/*tert*-butyl alcohol used for copolymer fractionations.  
<sup>c</sup> At 48% MA, the DTA maximum occurs at 160°C.

solubility parameter of the mixture is known together with data on one of the components, the solubility parameter of the second component can be derived.

Using a well characterized styrene-MA copolymer containing 5 mol % MA and having  $p = 1.067 \text{ g/cm}^3$ , Schneier<sup>(118)</sup> calculated  $\delta = 8.98$ . Suh and Corbett<sup>(113)</sup> experimentally determined  $\delta = 9.08$  for the same copolymer.

Molecular weight, thermogravimetric (TGA), differential thermal (DTA), and glass transition studies have also been run on both fractionated and unfractionated copolymers (Table 9.1). For a fractionated copolymer, with anhydride in the range of 7–13 mol %, the following relationship between number-average molecular weight and intrinsic viscosity holds:

$$[\eta] = 2.42 \times 10^{-4} (\bar{M}_n)^{0.652}$$

For unfractionated copolymer, with anhydride content in the 8–11 mol % range, the relationship between weight-average molecular weight and intrinsic viscosity appears as follows:

$$\begin{aligned} \bar{M}_w &= 4.98 \times 10^5 [\eta]^{1.426} \\ [\eta] &= 2.01 \times 10^{-6} (\bar{M}_w)^{0.702} \end{aligned}$$

In contrast, an unfractionated equimolar styrene-MA copolymer has the following viscosity-molecular weight relationship:

$$[\eta] = 0.7704 \times 10^{-4} (\bar{M}_w)^{0.725}$$

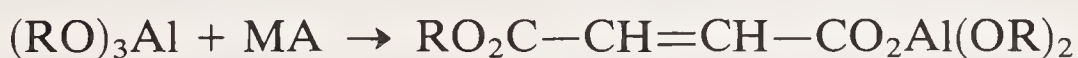
Since all viscosities were run in 2-butanone at 30°C, the results show that the equimolar copolymer is more expanded in the ketone solvent. A

summary of some additional properties for five unfractionated styrene-MA copolymers are shown in Table 9.1.

Both low and high molecular weight, nonequimolar styrene-MA copolymers have been explored for use in a variety of applications such as water-based coatings,<sup>(114-116,122,138)</sup> melamine-cured coatings,<sup>(122,135,139)</sup> floor polishes,<sup>(140)</sup> and foams.<sup>(257,531,532)</sup> Epoxy resins have been modified and cured with the copolymer to produce superior decorative coatings and laminates with good electrical properties.<sup>(110,111,141,142)</sup> Hydroxylamine derivatives of the copolymers, as ion-exchange resins, are capable of binding various heavy-metal salts.<sup>(112)</sup> Divinyl benzene-MA copolymers<sup>(143,144)</sup> also function very well as ion-exchange resins.<sup>(145-147)</sup> The sodium salts of these copolymers have received some attention as viscosity-reducing additives for oil well drilling needs.<sup>(148)</sup> Combinations of a 75-25 (styrene:MA) copolymer with 5% of a trifluoromethanesulfonates derivative of 3-bromo-2,2-bis(bromomethyl)-1-propanol can be used to prepare self-extinguishing, carbon-forming plastics.<sup>(149)</sup>

Styrene, MA, peroxides, and sawdust may be combined and polymerized to obtain useful wood-plastic composites.<sup>(150)</sup> In the effort, the hydroxyl groups on the cellulose react to some extent with the anhydride residues to give a three-dimensional structure, with very good moisture resistance. This concept could possibly be useful for improving the physical properties of many soft woods.<sup>(541)</sup>

Mixtures of styrene and MA, when combined with aluminum alkoxides or phenoxides, polymerize rapidly in air to give plastic materials.<sup>(151)</sup> Free-radical (peroxide) initiators may be used to accelerate the reaction, but are not necessary to obtain polymerization. The reaction also works with other vinyl monomers, such as vinyl toluene and methyl methacrylate. MA-aluminum alkoxide reactions are known to be highly exothermic, giving dark-colored solids (see Chapter 7). The crosslinked materials, with reduced flammability, have aluminum bridges between the polymer molecules. Presumably, the aluminum alkoxide and the anhydride reaction occurs as follows:



In this manner, depending on the alkoxide/anhydride ratio, alkoxy groups can be replaced with acyloxy groups, giving highly crosslinked composites. Variation of this concept has also been used by others to prepare plastic composites.<sup>(114)</sup>

High-molecular-weight styrene-MA copolymers with small amounts of MA are very useful in high-impact molding materials.<sup>(121-123,514,538)</sup> Dylark,<sup>(153,482)</sup> a product of Arco Polymers, and Cadon resins,<sup>(544)</sup> recently introduced by Monsanto, are such polymers.<sup>(153,482)</sup> These materials offer rigidity equivalent to many other thermoplastics and heat deflection temperatures of present products range between 230°F and 260°F, with higher



heat resins (Table 9.2) under development. The combinations of properties in Dylark and nitrile rubber modified Cadon resins often compare favorably with many other engineering type resins, yet these materials are available at reduced costs.<sup>(482,544)</sup> Since 1970, Dylark–glass fiber composites have experienced acceptance and growth in stamped rigid structural parts. Dylark has also been processed into foam laminate headliners for cars since 1977. Table 9.2 shows some of the properties of composites that may be obtained by reinforcing Dylark with glass fiber. If maleimide and *N*-phenylmaleimide become commercially available, one would expect these monomers to be used also to prepare marketable plastics of the same type.<sup>(507,508)</sup> Styrene–fumaric acid alkyl ester copolymers, prepared by emulsion or suspension polymerization techniques, also look useful as thermoplastics.

Various derivatives of the nonequimolar copolymers have also been studied in other applications. For example, hydroxyalkyl acrylate derivatives of the styrene–MA copolymer are potentially useful for the modification of unsaturated polyester formulations to give low shrink moldings and laminates<sup>(154)</sup> and in photocurable systems. Blends of copolymer containing 15–30% MA with glycidyl methacrylate and styrene may be molded or used to prepare laminates with low shrinkage, low softening, and good thermal deformation properties.<sup>(533)</sup> Copolymers with *N,N*-dialkylcarbamic ester groups are useful as dewatering aids for cellulose pulp.<sup>(152)</sup> Attention has also been given in recent times to preparing reactive polymers from styrene–alkyl glycidyl maleate and fumarate copolymers<sup>(500)</sup> and coatings from styrene–dialkyl fumarate copolymers.<sup>(505,506)</sup> The ARCO Chemical Company literature on SMA resins,<sup>(543)</sup> containing styrene:MA ratios of 2:1 and 3:1, gives properties, derivatives, and many possible uses for nonequimolar SMA copolymers.

### 9.2.2. Vinyl Chloride

Vinyl chloride (VC) readily copolymerizes with MA (see table in the appendix to this chapter) maleates and maleimides,<sup>(1)</sup> using free-radical initiators to give random copolymers.<sup>(155,156)</sup> The effect of MA on the chain-transfer constant ( $C_s$ ) during polymerization of vinyl chloride has been studied at 40–70°C.<sup>(157)</sup> At 60°C, the MA  $C_s$  was  $7.7 \times 10^2$ , compared to a styrene  $C_s$  of  $72.2 \times 10^2$ . Melville and Burnett<sup>(7)</sup> determined the copolymerization rate constant for the VC–MA pair to be  $2.1 \times 10^4 \text{ liter mol}^{-1} \text{ s}^{-1}$ . Several studies have shown that equimolar copolymers may also be obtained for the monomer pair (see Chapter 10). It has been observed that the presence of MA enhanced the polymerization rate of vinyl chloride.<sup>(158)</sup> As shown in the table in this chapter's appendix, vinylidene chloride also undergoes free-radical copolymerization with MA.<sup>(159)</sup>



Table 9.2 Glass-Fiber Reinforced Dylark Properties<sup>a</sup>

Property	Dylark <sup>b</sup>	Dylark 250 <sup>c</sup>
Tensile strength, psi	9 500	14 600
Flexural strength, psi	14 100	29 000
Flexural elastic modulus, psi	960 000	1 200 000
Izod impact strength, notched, ft. lb/in.	2.0	—
Deflection temperature under load (264 psi), °F	284	280

<sup>a</sup> From Reference 482.  
<sup>b</sup> Derivatized Dylark reinforced with 20 wt. % 1/4-in. chopped fiberglass strands.  
<sup>c</sup> Reinforced with 38 wt. % Fiberglass Mat.

It has long been recognized that a small amount (1–3 mol %) of MA helps stabilize poly(vinyl chloride)<sup>(160–163)</sup> and vinyl chloride copolymers against dehydrochlorination.<sup>(164,165)</sup> Maleic acid, alkyl maleates, dialkylstannyl dimaleates,<sup>(476,501,548)</sup> fumaric acid, and alkyl fumarates also retard thermal decomposition, with MA most effective. The thermal degradation of PVC was investigated in diethyl, dibutyl, and dioctyl maleate from 160 to 210°C.<sup>(497)</sup> The rate of dehydrochlorination was highest in dibutyl maleate and lowest in dioctyl maleate. Tin derivatives of MA have long been known as good stabilizers for PVC (see Chapter 3).<sup>(513)</sup> During thermal degradation HCl is eliminated and conjugated double bonds are produced. Also, the generated HCl promotes autocatalysis of the dehydrochlorination reaction. Color develops during dehydrohalogenation due to C=C generation. The activating influence of the conjugated double bonds is eliminated by the Diels–Alder reaction (see Chapter 4) of MA and the maleates with the conjugated double bonds. The presence of MA, alkyl maleates, and bis(triethylstannyl) maleate in the backbone of vinyl chloride copolymer does not provide the same effect.<sup>(496)</sup> The heat resistance of vinyl chloride–co–MA polymers, with both low to high levels of MA, are lower than that of PVC.<sup>(166,167)</sup> The copolymers are also more readily dehydrohalogenated by bases, such as pyridine,<sup>(156,168,169)</sup> attributed to the proximity of electronegative groups to the halogen in the polymer chain and availability of more-active  $\alpha$ -H atoms activated by the adjacent carboxyl carbonyl.

Vinyl chloride copolymers with a small amount of MA exhibit improved moisture absorption and good dyeability.<sup>(170)</sup> The patent literature discloses that these copolymers have potential uses in decorative coatings,<sup>(171–175)</sup> photographic films,<sup>(176,177)</sup> cellophane moisture-proofing coatings,<sup>(178,179)</sup> polymeric emulsifiers,<sup>(180,181)</sup> artificial leather coatings,<sup>(175,182,183)</sup> adhesives,<sup>(184,185)</sup> textile sizing,<sup>(186)</sup> and other applications.<sup>(187–191,530)</sup> PVC formulations containing a small amount of free anhydride are claimed to be useful in foamed plastisols

for insulation packaging, artificial leather, floor cushioning,<sup>(192,193)</sup> and strippable steel paints.<sup>(194)</sup>

Copolymers of vinyl chloride and lower alkyl maleates were at one time produced commercially both in Europe and the United States. Diethyl maleate copolymerizes readily with vinyl chloride, entering the polymer chain at a faster rate so that the maleic ester content of the polymer is higher than that of the comonomer feed.<sup>(1)</sup> Differential addition of maleic ester to the polymerizing mixture can be used to generate uniform copolymer. A copolymer containing 20% dimethyl maleate has good processing properties. Fumaric and maleic esters have fairly high boiling points and are difficult to remove from the resulting copolymers. This is objectionable, since the esters may volatilize during compounding operations. The latter fault, plus economic considerations, has caused this type of copolymer to be no longer commercially available. However, work continues in the area. For example, a recent patent<sup>(490)</sup> describes magnetic recording tapes prepared from a vinyl chloride:dimethyl maleate:diethyl maleate (80:10:10) terpolymer. Recent patents<sup>(280,378,517)</sup> also describe emulsion polymerization procedures for preparing vinyl chloride–maleate and vinyl chloride–maleimide copolymers useful in coatings and polymer alloys.

### 9.2.3. Vinyl Esters

The reactivity ratios in the table in this chapter's appendix shows that vinyl acetate (VA) readily copolymerizes with MA.<sup>(109,156,176,187,195–204)</sup> Other vinyl esters, such as vinyl abietate,<sup>(205)</sup> vinyl sterate,<sup>(206,207)</sup> vinyl perfluorobutyrate,<sup>(208)</sup> and vinyl 3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionate,<sup>(498)</sup> undergo facile free-radical-initiated copolymerization with MA (table in appendix to this chapter), maleates,<sup>(1,199,494,499)</sup> and fumarates<sup>(1,498)</sup> to give amorphous copolymers. In contrast to styrene, initiators are required to achieve copolymerization. Where the starting feed contains MA/VA ratios  $\geq 1$  and polymerization is  $<90^{\circ}\text{C}$ , the VA–MA pair copolymerizes to give a 1:1 alternating copolymer (see Chapter 10).<sup>(377)</sup> The UV-initiated copolymerization of the VA–MA pair also gives good yields of random copolymer.<sup>(133)</sup>

Hydrophilic VA–MA copolymers are readily soluble in water, alcohols, acetone, and aqueous alkaline solutions. Unlike styrene–MA copolymers, VA–MA copolymers form few precipitates with salts of heavy metals from aqueous solutions. Titration with sodium methoxide and thymol blue indicator may be used to determine percent anhydride residues.<sup>(198)</sup> Hydrolysis gives poly(vinyl alcohol–co–maleic acid) copolymer, which can be converted to materials with lactone rings.<sup>(203)</sup> In addition to being studied as polyelectrolytes,<sup>(209)</sup> nonequimolar VA–MA copolymers have been examined and recommended as fluid-loss control additives for drilling needs,<sup>(210)</sup> soil con-



ditioning agents,<sup>(109,211,212)</sup> adhesives,<sup>(156)</sup> detergent additive,<sup>(213–215)</sup> paper sizing,<sup>(216,540)</sup> PVC modifier,<sup>(217,218)</sup> emulsifier,<sup>(180,195)</sup> boiler scale removal agent,<sup>(214,219)</sup> and water treatment agent.<sup>(220)</sup> The alkali salt of a 95:5 vinyl acetate:maleate copolymer performs very well as a warp size for cellulose acetate yarns.<sup>(221)</sup> Treatment of the VA–MA copolymer with various monoazo food dyes could be useful for macromolecularization of food dyes.<sup>(475)</sup>

It was suggested that the copolymers are useful as coreactants in various thermosetting coating systems, but the use has never developed.<sup>(222)</sup> Hydrogels of the copolymers show excellent gel strength in the water-containing state.<sup>(196)</sup> Dialkyl maleates and fumarates, such as dibutyl maleate, when copolymerized with VA give materials used in both interior and exterior emulsion house paints.<sup>(200–202)</sup> The copolymers prepared from alkyl tin maleates look particularly attractive as a film-forming biocidal material, useful in antifouling paints.<sup>(479)</sup> The copolymers have lower flux temperatures, lower tensile strength, improved coalescence, and improved flexibility over VA homopolymers. Water-based coatings containing propyl, butyl, or isobutyl maleate copolymers with vinyl acetate have been crosslinked at 180°C, with various hardening agents to give coatings with impact strength of 35–50 kg/cm and high resistance to water.<sup>(486)</sup> It was recently claimed that coatings prepared from emulsions of poly(vinyl alcohol–dibutyl maleate) polymer mixtures give coatings having tensile strength at break of 131 kg/cm<sup>2</sup>, elongation at break 18%, covering power 65 g/cm<sup>2</sup>, and impact strength 50 kg/cm<sup>2</sup>.<sup>(534)</sup> The maleate<sup>(499)</sup> and fumarate<sup>(503)</sup> copolymers have also been known and marketed for some time as adhesives for the packaging, labeling, and textile-sizing industries. The hydrolyzed MA–VA copolymers are also useful as adhesives.<sup>(539)</sup> A copolymer with 28 wt. % dibutyl maleate is a very effective covering agent for typing errors.<sup>(510)</sup> Slow growth and market erosion has occurred in the coatings area, due to competition of VA–acrylate copolymers. Health aspects of the maleate-modified vinyl acetate copolymers was recently investigated, showing the copolymers should offer no problems.<sup>(474)</sup>

Other substituted vinyl acetates have also been copolymerized with MA. For example,  $\alpha$ -cyanovinyl acetate–MA mixtures copolymerize with peroxide initiators to give random copolymers.<sup>(223)</sup> The  $Q = 1.17$  and  $e = -1.06$  values for  $\alpha$ -cyanovinyl acetate suggests this monomer should strongly form a charge-transfer complex with MA (see Chapter 10) and give a 1:1 copolymer. However, various feed ratios of the two monomers failed to produce a 1:1 copolymer but gave only materials with a substantial excess of the acetate.

#### 9.2.4. Acrylonitrile

Free-radical-initiated copolymerization of MA with acrylonitrile has been investigated under both bulk<sup>(224)</sup> and solution<sup>(217,225)</sup> conditions. In solution, the copolymerizations were studied under both heterogeneous (benzene,



dichloroethane, ethyl acetate) and homogeneous *N,N*-dimethylformamide (DMF) conditions. Even though a charge-transfer complex forms between the two monomers (see Chapter 10), copolymerization follows classical Mayo–Lewis copolymerization concepts to give random copolymer. Materials that complex with MA, such as zinc chloride, DMF, mesitylene, anisole, cumene, naphthalene, pyridine, and tetrahydrofuran, promote both MA incorporation and copolymerization of the two monomers, but fail to bring about production of equimolar copolymers. The physicochemical properties of the MA–acrylonitrile copolymers have not been investigated. Random copolymers are also obtained from UV-initiated copolymerizations of the monomer pair in both dioxane or benzene.<sup>(133)</sup> The presence of MA and dioxane increased the rates of polymerization, but decreased the degree of polymerization of the copolymers with both a MA feed increase or increase of the amount of dioxane solvent.

Clear, cast rods of poly(acrylonitrile–co–MA), with 1–15% anhydride, have been prepared.<sup>(224)</sup> Properties of the castings were not reported. The MA–acrylonitrile copolymers have been claimed to be useful as a polyelectrolyte soil conditioner,<sup>(226)</sup> polyacrylonitrile (PAN) stabilizer,<sup>(227,228)</sup> molding resin additive,<sup>(229)</sup> antistatic additive,<sup>(230)</sup> cation-exchange resin,<sup>(231)</sup> and sizing agent for various textiles.<sup>(232)</sup> There are claims that MA, maleimide, and other MA derivatives perform as stabilizers for polyacrylonitrile materials.<sup>(223,234)</sup> The inhibiting action is thought to result from the nucleophilic addition of the initiator which catalyzed the “zipper” reaction to the inhibitor.

### 9.2.5. Acrylic Acid

Very little attention has been given to the production and evaluation of acrylic or methacrylic acid–MA copolymers. Some studies have shown that the acrylic acid–MA pair can be copolymerized to a 1 : 1 alternating copolymer, under the condition where MA concentration exceeds the acrylic or methacrylic acid concentration in the starting mixtures (see Chapter 10). Radiation-initiated, solid-state copolymerization of eutectic mixtures of acrylic acid with MA have been investigated by examination of phase diagrams, viscosities, and surface tensions of the binary mixtures.<sup>(235)</sup> Molecular interactions between the two monomers and crystal dislocations accelerate the polymerization rate. The physical and chemical properties of the copolymers have not been explored.

Zinc oxide–magnesium oxide blends of the acrylic acid copolymer can be used to prepare dental cements.<sup>(236)</sup> Blends of polyacrylic acid or acrylic acid–maleic acid copolymer and 7–25% free maleic acid are also claimed useful as aqueous setting solutions for dental glass ionomer cements.<sup>(477)</sup> Mixtures of the aqueous setting solution and dental cement powders give fast setting, high strength (1 400–1 500 kg/cm<sup>3</sup>), translucent cements, with an

appearance close to natural teeth. The methacrylic acid copolymer has been examined and shown very useful in adhesives to join hydrophilic materials to hydrophobic surfaces<sup>(237)</sup> and as esthetically pleasant dental cements for permanent fillings.<sup>(478)</sup> Other possible uses for the acrylic acid copolymer include detergent builders,<sup>(238)</sup> resist printing paste additive,<sup>(239)</sup> synthetic membranes,<sup>(240)</sup> and calcium carbonate dispersant for paper coatings.<sup>(241,242)</sup> Aqueous solutions of the acrylic and methacrylic acid copolymers are also good dispersants for aluminum hydroxide<sup>(243)</sup> and boiler scale inhibitor agents.<sup>(519)</sup> Copolymers of 2-chloroacrylic acid-MA have also been prepared and shown useful as detergent builders.<sup>(244)</sup>

### 9.2.6. Acrylic and Methacrylic Esters

Methyl, ethyl, butyl, 2-ethylhexyl, isooctyl, 2-hydroxyethyl, etc., acrylates<sup>(245-251)</sup> and methacrylates<sup>(64,249,252-256,258-268,529)</sup> copolymerization with MA have received substantial attention, as shown in the table in the appendix to this chapter and the patent literature. Maleate and fumarate copolymerizations with acrylates and methacrylates have also received substantial study.<sup>(1)</sup> The many patents in this area are mainly concerned with preparing coatings. Free-radical-initiated bulk polymerization of alkyl methacrylates may be accomplished with good control at 80–140°C by first charging the reactor with 5–15 wt. % 4-12C dialkylmaleate or fumarate esters.<sup>(535)</sup> The copolymers are useful as lubricating, wetting, or flowing agents for powder coatings.

Acrylic esters-MA monomer mixtures are generally polymerized in solution, with BPO or azobisisobutyronitrile (AIBN) initiators. The highest rates of copolymerization are observed in heterogeneous phase systems, where the difference in the solubility parameter of the solvent and the copolymer is  $\geq 1.4$  Hildebrand.<sup>(30)</sup> The copolymerization rate constant for the methyl acrylate-MA pair, at 25°C, has been estimated as  $588 \text{ liters mol}^{-1} \text{ s}^{-1}$ .<sup>(7)</sup> For comparison, the copolymerization rate constants for the styrene-MA, methyl methacrylate-MA, and vinyl acetate-MA pairs<sup>(7)</sup> are, respectively, 505, 40, and  $1.8 \times 10^4 \text{ liters mol}^{-1} \text{ s}^{-1}$ .

Photochemical (UV) initiated copolymerizations of MA with acrylates and methacrylates progresses well in benzene or dioxane, even without added photoinitiators.<sup>(133)</sup> With UV initiation, the molecular weight of the copolymers decreased with an increase of MA in the comonomer feed. Also, the rate of copolymerization increased but the molecular weights decreased as the concentration of dioxane in the comonomer solution increased. As expected, mercaptans are useful chain regulators to obtain low-molecular-weight materials.

The glass transition temperature ( $T_g$ ) of the methyl acrylate-MA copolymers have been obtained for materials with 8.0–43.7 mol % anhydride.<sup>(249)</sup> Over this range,  $T_g$  varied from 28.3 to 119.6°C. The results were discussed



in terms of the chain stiffeners. Volume expansion of the copolymers in the glassy and rubbery states decreased with increasing MA content. The product of  $T_g \Delta\alpha$  (where  $\Delta\alpha$  is the difference in volume expansion above and below  $T_g$  and equal to 0.093 for the methyl acrylate copolymer) was nearly constant, regardless of the composition.

The patent literature claims that methyl, ethyl, and butyl acrylate-MA copolymers are useful in a variety of coatings, such as enteric,<sup>(269,270)</sup> water-borne,<sup>(250,251)</sup> thermosetting,<sup>(271-273)</sup> electrodeposition,<sup>(274)</sup> antistatic,<sup>(275)</sup> photographic,<sup>(276)</sup> textile,<sup>(277)</sup> and wool shrinkproofing<sup>(278)</sup> applications. In addition, some of the compositions have shown possible use as wet-strength additives for paper,<sup>(279)</sup> coatings for a macroporous polysulfone-polyester membrane useful in desalination applications,<sup>(516)</sup> textile sizing,<sup>(280)</sup> binders for charcoal deodorants,<sup>(281)</sup> water softening agents,<sup>(220)</sup> impact modifiers for thermoplastics,<sup>(282)</sup> inorganic pigment dispersants,<sup>(283,284)</sup> hot melt, and other adhesives<sup>(285-287)</sup> applications. Ethyl acrylate-co-MA adhesives exhibited high thermal resistance to aluminum metal, and blends of the copolymer with epoxy resins gave superior thermosetting metal adhesives.<sup>(245,246)</sup> Thinking of thermal stability, it is known that free anhydride will slightly lower the heat resistance of acrylate polymers.<sup>(247)</sup> In contrast, the photochemical stability of acrylate polymers may be significantly enhanced by tetrahydrofuran or 1,4-dioxane charge-transfer complexes of MA.<sup>(248)</sup> Long-chain, isooctyl, 2-ethylhexyl, etc., alkyl acrylate-MA copolymers are useful in preparing lubricant additives, aerosol spray adhesives, microsphere coatings, and other uses.<sup>(288-291)</sup>

The patent literature discloses that several speciality-type acrylate monomers, such as  $\beta$ -hydroxyethyl acrylate,<sup>(292,293)</sup> 2-acryloyloxyethyl phenyl carbonate,<sup>(294)</sup> vinyl acrylate,<sup>(295)</sup> 2,2,2-trifluoroethyl acrylate,<sup>(296,297)</sup> *N,N*-dimethylaminoethyl acrylate,<sup>(298,299)</sup> glycidyl acrylate,<sup>(300)</sup> cyanoacrylates,<sup>(301,485)</sup> and several diacrylates,<sup>(302)</sup> have been copolymerized with MA. These copolymers were shown to exhibit properties which allowed the materials to be useful for polymeric emulsifiers,<sup>(292)</sup> adhesives,<sup>(294,298)</sup> printing pastes,<sup>(295)</sup> fire retardant textile coatings,<sup>(296)</sup> and fibrous structural materials.<sup>(302)</sup> Maleate and fumarate copolymers with acrylates also show possible utility in coatings, dispersants, adhesives, and other applications.<sup>(303-305)</sup> Cyanoacrylate adhesives have much improved heat resistance and adhesion to steel when modified with a small amount (0.06–1.2%) of MA and chloromaleic anhydride,<sup>(301)</sup> maleic acid,<sup>(522)</sup> and dialkylmaleates.<sup>(523,524)</sup>

A recent patent<sup>(484)</sup> describes an excellent technique for radical-initiated bulk copolymerization of acrylates with maleates and fumarates. The heat of the copolymerization—i.e., acrylate polymerization—reaction is regulated by addition at 80–140°C of 85–95% acrylic monomer(s) containing a radical initiator to 5–15% C<sub>4</sub>-C<sub>12</sub> fumarate or maleate, so that the amount of free



acrylate at any time is  $<20\%$ . As an example, a 90:10 butyl acrylate: diisobutyl fumarate copolymer was prepared in a 97.8% yield with limiting viscosity number of 37.1 ml/g (1% in  $\text{CHCl}_3$ ).

Methyl methacrylate–MA copolymerizations and property studies of the copolymers have also received substantial attention.<sup>(30,64,249,254,255,258–260, 262–266,268,307,542)</sup> Conditions have been developed for preparing alternating (1 : 1) copolymers of methyl methacrylate–MA (see Chapter 10). However, typical copolymerization conditions produce random copolymers. Binary mixtures of the monomers have been copolymerized in solution, with peroxide initiators at 60°C and at pressures  $\leq 4\,000$  atm. In benzene solvent, the specific viscosity ( $\eta_{sp}$ ) of the copolymers varied from 1.10 to 5.27, as pressure increased from 1 to 4 000 atm. The composition of the copolymers was almost independent of pressure. The rates of copolymerization under these conditions increased from 4.34 to 194.0 %/h.<sup>(64)</sup> The copolymerization rate constant for the pair,<sup>(7)</sup> at 25°C, has been estimated as 40 liters  $\text{mol}^{-1} \text{s}^{-1}$ . The rate increase, which results from increasing chain propagation rate constants ( $R_p$ ) with increasing pressure, was of the same order observed for homopolymerization of methyl methacrylate.

The copolymerization of methyl methacrylate with MA displays unusual features that are connected with the termination mechanism. Kinetic studies in benzene at 60°C showed that the rate increased with an increasing mole fraction of anhydride,<sup>(61,260)</sup> which is not in accordance with normal copolymerization theory. Results from a separate kinetic study run in ethyl acetate,<sup>(259)</sup> in which both the monomers and copolymer are soluble, showed no such rate maximum. In both heterogeneous-phase (benzene) and homogeneous-phase (acetone) systems, Tsang<sup>(30)</sup> showed that the maximum rates of copolymerization occurred at 1 : 1 feeds. The copolymerization rates were always greatest under heterogeneous-phase conditions. The increase in rate with increasing solution viscosity shows diffusion control of the termination step. Also, the termination rate constant ( $k_t$ ) decreased with increasing anhydride content, with a maximum drop in the  $k_t$  (Table 9.3) at an anhydride mole fraction between 0.07 and 0.12.<sup>(259)</sup> The glass transition temperature ( $T_g$ ) of the copolymer also shows a maximum in this range (Table 9.3).

Kinetic studies of the solution (benzene) and bulk polymerization of methyl methacrylate with MA have been run at 60°C and 70°C, using AIBN initiator. The microstructure of the purified copolymers was determined by  $^1\text{H}$ -NMR and IR spectroscopy. Analysis of the comonomer pair sequence distribution for the solution-prepared copolymers supported a copolymerization mechanism involving participation of an association species between the two monomers.<sup>(260)</sup> A terminal model or the classical Mayo–Lewis<sup>(6,21)</sup> concept more adequately explained the results of bulk copolymerization, where the comonomer sequence distribution was more random. Theoretically, the concentration of associating species should be greatest in bulk, which was

Table 9.3. Methyl Methacrylate–MA Copolymerizations<sup>a</sup>

Copolymer anhydride mole fraction	$k_t$ (relative)	$T_g$ , (°C) dilatometric	$T_g$ , (°C) vibrating reed
0.00	1.0	95	85
0.02	—	95	—
0.05	0.20	111	—
0.07	0.08	96	115–120
0.19	0.17	113	125

<sup>a</sup> From Reference 259.

contrary to experimental observations. Since the formation constant for the complex should decrease with an increasing dielectric constant, increases of MA in the feed could bring about a decrease of the formation constant. This being true, the concentration of the associating species was substantially reduced in bulk, exerting negligible effect on the copolymerization.

The  $T_g$  of methyl methacrylate–MA copolymers have also been studied over the broad range 8.4–49.8 mol % anhydride.<sup>(249)</sup> Analogous to the acrylated system,  $T_g$  increased with MA content in the copolymer. Using a dilatometric technique, the  $T_g$  of the copolymers over this range varied from 118.5 to 147.0°C. The results were discussed in terms of the chain stiffness of each copolymer. The product of  $T_g\Delta\alpha$ , where  $\Delta\alpha$  is 0.107, was nearly constant regardless of the copolymer composition.

The reactivity ratios measured for the methyl methacrylate–MA copolymerizations vary considerably, depending on the homogeneity of the systems studied (see table in the appendix to this chapter).<sup>(60)</sup> The reactivity ratio of the methacrylate varied as follows (solvent,  $r_1$ ): cyclohexane, 0.50; carbon tetrachloride, 0.90; toluene, 3.10; chloroform, 3.85; tetrahydrofuran, 3.40; and 2-butanone, 3.85. Progressing through the solvents, the copolymer was insoluble in cyclohexane and most soluble in 2-butanone. The copolymers obtained in cyclohexane and carbon tetrachloride had a larger MA content than the copolymers obtained in the homogeneous or bulk polymerization systems. Polymerization must be enhanced in the precipitated polymer to explain this observation, due to enhanced MA absorption on the copolymer. In the dilute homogeneous systems, the relation  $R_p$  (rate of polymerization) =  $\alpha[M][I]^{1/2}$  was observed at [methacrylate]/[MA] = 1. In short, chain transfer to MA was predominant and the degree of polymerization was controlled by the [methacrylate]/[MA] ratio.

Several techniques have been examined for determining the anhydride content and structural effects of the macromolecular chain on the reactivity of the anhydride moiety for the acrylate – MA and methacrylate–MA copolymers.<sup>(254,255,258,259)</sup> The anhydride content is readily determined potentiometrically with sodium methoxide and phenolphthalein indicator.<sup>(258)</sup> It is



very important to take care to rid the copolymer of free MA, by reprecipitation, washing, dialysis, or other techniques, since the anhydride is very strongly absorbed by the copolymer.<sup>(259)</sup> Using aniline and *p*-toluidine, aminolysis studies of the methyl methacrylate copolymer was carried out in benzene and followed by UV spectrometry. Compared to the succinic anhydride-amine reaction, the copolymer amine reaction velocity was slower than expected.<sup>(255)</sup> This was attributed to lack of good solubility of the copolymer in benzene and shielding of the anhydride moiety from the amine. Light-scattering studies show the anhydride groups cause contraction of the polymer molecules in the benzene solution,<sup>(258)</sup> i.e., copolymer coiling increases with the number of anhydrosuccinic anhydride groups.<sup>(254,255)</sup> The methacrylate chain residues form a shield around the anhydride groups, which are less soluble and therefore gather into the center of polymeric coils, decreasing accessibility. Condensation reactions of the MA-methyl methacrylate inter-polymer with glycols in the molten state have been examined by a plastograph technique.<sup>(512)</sup> Crosslinking was monitored by the increase of viscosity.

Gamma-irradiated methyl methacrylate-co-MA polymers have been studied by electron spin resonance (ESR) spectroscopy.<sup>(264,266,268)</sup> The ESR spectra, over the range  $-50^{\circ}\text{C}$  to  $+50^{\circ}\text{C}$ , varied with both temperature and the anhydride content of the copolymers. The spectra were completely different than that for  $\gamma$ -irradiated poly(methyl methacrylate). Formation and decay of the generated free radicals were discussed and explained.<sup>(264,268)</sup>

The electrostatic properties of methyl methacrylate-co-MA polymers have been examined in fair detail.<sup>(262,263,265)</sup> The relationship between the static electrification, chemical structure, chargeability, etc., were explored and discussed. The electrostatic charge decay of the copolymer was comparatively large and the maximum charge decreased with increasing temperature, whereas in poly(methyl methacrylate) the charge decay is very small and the maximum charge is not influenced by temperature. The charge curve of the copolymers exhibited the characteristic S shape. It was also shown that the electrification of the copolymer was determined by the energy levels of the polymer units and their interaction.

High-molecular-weight methyl methacrylate-MA copolymers<sup>(306)</sup> have potential use as coatings and plastics.<sup>(296,303,307,308,546)</sup> Some of the copolymer compositions are useful as modifiers for alkyd coatings,<sup>(256,267)</sup> gelatin for photographic films,<sup>(261,309)</sup> dispersant for silver halide emulsions,<sup>(310)</sup> and other polymeric dispersant<sup>(311,515)</sup> applications. The copolymer has also been examined as a thiamine carrier for medicinal application,<sup>(312)</sup> PVC foam modifier,<sup>(313)</sup> and a boiler scale removal agent.<sup>(214)</sup> Ester derivatives of the copolymer have also been found useful as lubricant additives.<sup>(314)</sup> Solutions of either the methyl or ethyl methacrylate copolymers dissolved in alcohols and neutralized with ammonia are claimed to be useful for processing photographic films.<sup>(276)</sup> The copolymer containing 15 mol % MA physical properties



have been compared with poly(methyl methacrylate). Incorporation of 15% MA increases the compressive strength, Rockwell hardness, and density of the polymer, with no loss of tensile strength, shear hardness, or mar resistance of the base polymer. Metal salts of the 15:85 MA–methyl methacrylate copolymer, with several different cations, have been briefly examined as ionomer (ion containing) type films.<sup>(252,253)</sup> Clear films may be obtained that exhibited improved shear hardness, scratch and solvent resistance, and light transmission, when compared to unmodified copolymer. Poly(methyl methacrylate) has a shear hardness ( $G$ ) of 600 and 74% light transmission. In comparison, 15 mol % MA copolymer modified with  $K^+$ ,  $NH_4^+$ ,  $Mg^{2+}$ ,  $Fe^{3+}$ ,  $Cr^{3+}$ , and  $Al^{3+}$  exhibited, respectively,  $G$  values of 900, 600, 700, 900, 1 100 and 1 100, and light transmission values of 62.5, 82.0, 84.5, 73.0, 69.6, and 71%.

Copolymers derived from methacrylic esters of long-chain alcohols, such as lauryl, stearyl, and dodecyl, may be modified to give useful lubricating and fuel oil additives.<sup>(315–319)</sup> As an example, equimolar quantities of lauryl methacrylate and MA were copolymerized for 6 h in refluxing benzene with BPO initiator. Post reaction of the methanol-precipitated polymer with octodecyl alcohol and dibutylamine provide an oil-soluble derivative useful as an antisludging additive for fuel oils.<sup>(315)</sup>

Specialty methacrylates, such as the glycidyl,<sup>(300,320,321)</sup> 2-hydroxyethyl,<sup>(322)</sup> 2,4,6-tribromophenyl and tribromoneopentyl,<sup>(323)</sup> 4-methyl-6-hydroxymethyl-pyrone-2,<sup>(324)</sup> 2-cinnamoyloxyethyl,<sup>(325)</sup> the *l*-menthyl,<sup>(326)</sup> and benzyl ester<sup>(549)</sup> have also been copolymerized with MA. The copolymers were shown potentially useful as epoxy resin modifiers, antistatic coatings, flame-retardant additives, and photoreactive coatings. Uses for optically active copolymers prepared from *l*-menthyl methacrylate have not been examined.<sup>(326)</sup>

Dimethylamino (DMAM) and diethylaminoethyl methacrylate (DEAM) copolymerization with MA have received some study.<sup>(298,299,327–329)</sup> Neat copolymerizations of the monomer pairs at 30°C produce blackish, brown, tarry materials<sup>(327)</sup> Copolymerization of DMAM with MA in acetone, benzene, dioxane, and toluene, using typical free-radical initiators, gave only dark-colored solutions with very little detectable polymer. Solution copolymerization of DEAM with MA, in the presence of radical initiators, progresses more readily to give copolymer. Aqueous copolymerization of the two monomers with MA are exothermic. Copolymerization of DMAM with MA has been explored as a method to prepare polyampholytes.<sup>(329)</sup> Light-scattering studies indicated that extensive aggregation of the copolymer exists in aqueous solution. Aqueous solutions of the DEAM copolymer showed both the amphoteric and cathophoretic mobilities of a magnitude dependent on the concentration of the tertiary amine and carboxyl groups in the copolymers and their ionization.<sup>(328)</sup> Deviations for the ionization equilibrium in both

directions from the isoelectric point increased the viscosity, optical density, and electrophoretic mobility of aqueous solutions of the copolymer. At pH 8.5 and 6.8 an inversion occurred in the potential signs of the copolymer.

Nucleic acids, such as uracil, thiamine, adenine, and L-proline<sup>(330,331)</sup> and 1-phenyl-2-aminopropane,<sup>(332)</sup> have been treated with methacryloyl chloride to prepare monomers. These modified methacrylamides may be copolymerized with MA to provide novel, potential drug carrier resins. This type of chemistry should also be exploitable to prepare water-soluble food dyes<sup>(475)</sup> and artificial sweeteners as well as deliver herbicides and pesticides in the agricultural industry.

Trialkylmethacryloyloxystannanes-MA copolymers have been prepared and their physical, chemical, and antimicrobial properties examined.<sup>(333)</sup> Copolymers containing  $(\text{CH}_3)_3\text{Sn}$ ,  $(\text{CH}_3\text{CH}_2)_3\text{Sn}$ ,  $(\text{C}_6\text{H}_5\text{CH}_2)_3\text{Sn}$ , etc. groups exhibit good bactericidal and fungicidal properties in coating formulations.<sup>(334)</sup> On exposure to UV ( $\lambda = 205 \text{ nm}$ ), these copolymers undergo complex supermolecular transformations, giving crosslinked coatings or films.<sup>(537)</sup>

Dimethacrylate derivatives of polyols copolymerize with MA to give crosslinked materials.<sup>(335,336)</sup> These resins are potentially useful as cation-exchange and drug carrier resins.

### 9.2.7. Acrylamide

Maleic anhydride-acrylamide monomer mixtures have been copolymerized in the solid phase with  $\gamma$  rays ( $^{60}\text{Co}$ )<sup>(337-339)</sup> and in polar solvents with free-radical initiators.<sup>(340)</sup> Methods to determine molecular weights of the copolymer have been discussed recently.<sup>(341)</sup> It has also been shown that MA/acrylamide molar ratios  $\geq 1$  can be polymerized to give an alternating copolymer (see Chapter 10). MA has also been copolymerized with *N*-(1,1-dimethyl-3-oxybutyl) (diacetone) acrylamide,<sup>(342)</sup> *N-tert*-amylacrylamide,<sup>(337)</sup> *N,N*-diphenylacrylamide,<sup>(343)</sup> and *N*-isopropylacrylamide.<sup>(344)</sup> Acrylamide also copolymerizes with fumarates when exposed to  $\gamma$  radiation.<sup>(337)</sup>

Acrylamide forms eutectic mixtures with MA, having mixed crystals. Rates of cooling of the fused mixtures of the two monomers exerts a marked influence on the degree of conversion after  $\gamma$  irradiation.<sup>(338)</sup> Copolymerization rates were higher in the liquid melt than in the presence of a crystalline phase.<sup>(339)</sup> Independent of the initial monomer mixtures and the degree of conversion, copolymers formed in the solid phase were almost wholly of a composition corresponding to the initial feeds, independent of the initial monomer mixtures and the degree of conversion. The effect was repeated systematically, even when the rate of homopolymerization of one of the monomers in the solid phase was greatly in excess of that of the other monomer.<sup>(337)</sup> Patents disclose these copolymers are potentially useful as



flocculants.<sup>(345,346,349)</sup> The methacrylamide-MA copolymer has also been studied for purification of industrial waste water.<sup>(536)</sup> The disodium salt of MA has been copolymerized with the sodium salt of 2-acrylamido-2-methylpropanesulfonic acid, using peroxide initiators, to give useful dispersant and deflocculants for water-insoluble compounds of Fe, Ca, Al, and for silt and clay particles.<sup>(493)</sup> The copolymers also prevent boiler scale formation, corrosion, etc., without being affected by the hardness of the water.<sup>(519)</sup> Copolymers prepared in aqueous solutions are claimed to be useful in well wall materials, coatings for microcapsule production, and for paper dry-strength agents.<sup>(347,348,545)</sup>

A mixture of acrylamide, MA, urea, and water (50 : 30 : 10 : 10) was melted to form a uniform mixture and exposed to radiation to obtain a hard opalescent resin. Heating at 70°C decomposed the urea and expanded the resin by a factor of 44 to give a rigid, crosslinked foam.<sup>(350)</sup>

Nonequimolar *N*-vinyl-2-pyrrolidone-MA copolymers have had some study. The copolymers are generally prepared in the same manner as the homopolymers of the *N*-vinyl lactams and have similar properties with respect to water solubility. A copolymer containing 80% by weight of MA is a useful coating for water-dispersible particulate organic polymers. Such coated polymers have enhanced dispersibility in aqueous solutions with a minimum of agglomeration of the water-soluble polymer.<sup>(491)</sup>

It is possible that *N*-vinyl-2-pyrrolidone-MA copolymers offer routes to a variety of chromatographic and controlled release applications. Supporting this thought,  $\gamma$ -aminopropylated macroporous silica has been treated with *N*-vinyl-2-pyrrolidone-MA copolymers and then with 2-mercaptoethyl-amine to prepare a carrier for disulfide exchange covalent chromatography of proteins.<sup>(520)</sup>

### 9.2.8. Acrolein

Copolymerization of acrolein-MA mixtures are readily achieved with free-radical initiators.<sup>(351,352)</sup> Copolymerization of a 90:10 (acrolein:MA) mixture in water with *tert*-butyl peroxide produces a high-molecular-weight, water and acetone insoluble product. Copolymers prepared with 20, 30, and 45 wt. % MA are also water insoluble. Copolymers could easily be prepared with inherent viscosities (determined in aqueous caustic) over the range 0.5–5.0 dl/g. Over this range, the light scattering molecular weights vary from 100,000 to 3,000,000. Dilute, aqueous caustic solutions of the 90:10 copolymer could be applied to cotton fabric, by conventional padding techniques, to give materials with improved abrasion resistance, with good fabric lay.<sup>(351)</sup> The water-soluble sulfonic acid derivative of the same copolymer gave increased strength and abrasion resistance to kraft paper. The copolymers could be treated with alcohols, using acid catalysts, to give plastics. The molded



transparent, flexible plastics were potentially useful in a variety of applications.  $\alpha$ -ethylacrolein also undergoes free-radical copolymerization with MA.<sup>(352)</sup> These copolymers are claimed to have properties useful for metal complexing agents.<sup>(352)</sup>

### 9.2.9. Vinylsulfonic Acid

Vinylsulfonic acid,<sup>(353,354)</sup> methallylsulfonic acid,<sup>(354)</sup> and 2-methyl-2-propene-sulfonate,<sup>(355)</sup> in the presence of free-radical initiators, readily copolymerize with MA. The patent literature claims these copolymers are useful as detergent builders.<sup>(354,355)</sup> Blood anticoagulating properties of the vinylsulfonic-MA (acid) copolymers, containing 48 and 95 mol % sulfonate, have also been examined by Gregor.<sup>(353)</sup> The copolymers exhibited some reduced anticlotting activity, compared to the homopolymer of vinylsulfonic acid. Given study, it may be found that the copolymers are also useful in other biomedical areas and especially in catalysis and boiler scale prevention applications. With regard to the latter suggested application, it is noted that the 1:3 MA-styrene sulfonic acid copolymer is known for inhibiting boiler scale formation in aqueous media.<sup>(518)</sup>

### 9.2.10. Allyl Monomers

Allyl monomers, such as allyl acetate (see Chapter 10), are often known to give 1:1 alternating copolymers with MA.<sup>(356)</sup> However, several polyfunctional allyl compounds, such as allyl ethers, allyl malonates, and allyl carbonates, have been combined with nonequimolar amounts of MA and polymerized with free-radical initiators to give casting compositions, coatings, and adhesives.<sup>(357-363)</sup> A 70:30 mixture (wt. %) of diethylene glycol bisallyl carbonate (CR-39) and MA forms a 100% reactive syrup that can be cured with peroxides to give clear castings.<sup>(359)</sup> Castings made from this type combination have been evaluated in contact lens formulations and other castable plastics.<sup>(357,358)</sup>

Schildknecht<sup>(356)</sup> explored copolymerization of triallyl cyanurate (TAC) and triallyl isocyanurate (TAIC) with MA. The red-colored acetone solution of the TAC-MA copolymer could be neutralized with aqueous sodium hydroxide to give a white opaque microgel dispersion. The dispersion could be used to cast free films.

Using high-energy radiation, dimethylallyl has been copolymerized with MA to give crosslinked materials.<sup>(356)</sup> These materials were suggested as possible ion-exchange resins.

Allyl alcohol is known to copolymerize with MA to give equimolar copolymers with lactone and carboxylic acid groups (see Chapter 10). Allyl maleate or fumarate, with free-radical initiation, will also copolymerize with

MA, giving nonequimolar copolymers potentially useful in detergent compositions.<sup>(521)</sup>

### 9.2.11. Olefin Monomers

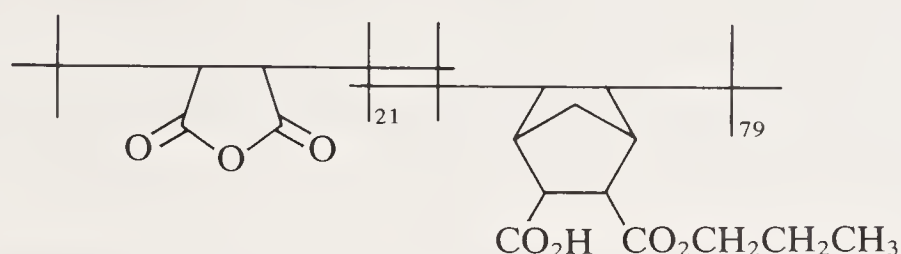
As a general rule, olefin-MA copolymerizations, run in the presence of free-radical initiators, give only equimolar copolymers (see Chapter 10). However, conditions are known where random copolymers may be prepared that contain less than equimolar amounts of MA. For example, high-pressure, free-radical-initiated copolymerization of ethylene with 3% MA or 2–3% monomethyl maleate has been used to prepare ionomer-type materials.<sup>(364–366)</sup> These materials are somewhat similar to the well known Surlyn A ionomer polymers.<sup>(367)</sup> Copolymerization of dialkyl maleates with ethylene at high pressure, with free-radical initiators, also produces random copolymers,<sup>(368)</sup> with  $\bar{M}_n = (3.10–3.67) \times 10^5$ . The patent literature also describes techniques for emulsion polymerization of dialkyl maleate-ethylene copolymerizations, at pressure up to 200 atm to obtain dispersions of high-molecular-weight copolymers with good film-forming characteristics. The products with low carboxylic acid content appear to be useful in textile and paper manufacturing efforts. High-pressure copolymerization of cyclopentene with MA has also received some study.<sup>(369)</sup> The copolymer compositions were affected by pressure; i.e., for a given feed composition the content of olefin in the copolymer increased with pressure.

Maleic acid copolymerizes with ethylene, but with great difficulty. A continuous bulk process, run at 210–220°C, pressures of 1 350–1 450 atm and with 0.05–0.2% *t*-butyl proxyacetate, gives after an 8-min residence time in the reactor a copolymer with maleic acid content of 0.14–0.9%.<sup>(370)</sup> An emulsion process, run without emulsifier, in 19% aqueous *t*-butanol at 100°C with persulfate initiator, gives nonequimolar copolymer.<sup>(371)</sup> The copolymerization of monoalkyl maleates with ethylene has also been achieved to give ethylene-rich copolymers.<sup>(372)</sup> The 76:24 (mol %) copolymer was found useful as a lubricant for spinning nylon fibers. It is worth noting that MA retards charring and crosslinking in the thermal degradation of high-molecular-weight polyolefins to produce polyolefin waxes.<sup>(373)</sup> Copolymerization of ethylene with ethyl glycidyl maleate or fumarate has been explored as a method for preparing reactive polymers.<sup>(500)</sup>

Esters of endomethylene tetrahydrophthalic anhydride and other derivatives of norbornene are known to form eutectic mixtures with MA.<sup>(55,70,72,73,340,341,374–379)</sup> Solid-state copolymerization of the eutectic mixture of monopropyl endomethylene tetrahydrophthalate and MA, using <sup>60</sup>Co  $\gamma$ -ray initiation, produces nonequimolar copolymer.<sup>(374)</sup> Neither monomer homopolymerizes under the experimental conditions used. It is believed that copolymerization of the monomer mixture is made possible by the increased



mobility of the monomer molecules at the crystal interfaces. In fact, copolymerization was assumed to occur only at these interfaces. The copolymer composition and structure is shown as follows:



Conventional Ziegler-type catalysts, containing alkylaluminum– $\text{TiCl}_3$  combinations, have been modified with MA for the polymerization of various olefins.<sup>(384,385,390)</sup> To prevent killing the catalyst activity, MA is used in an amount corresponding to 0.5 mole per mole  $\text{TiCl}_3$ . MA modified organocatalysts containing tungsten hexachloride have also been used to polymerize cyclic olefins.<sup>(386,387)</sup> In contrast, modified Ziegler-type catalysts containing alkylaluminum halides, such as ethylaluminum sesquichloride and  $\text{VCl}_3$ , are claimed to remain active in the presence of polar monomers such as MA. This type catalyst system has been used to copolymerize MA with several olefins or olefin mixtures, including propylene and cyclopentene, dicyclopentadiene, ethylidenenorbornene, ethylene-propylene, ethylene-propylene-1,4-hexadiene, *cis*-piperylene-*trans*-piperylene, dicyclopentadiene-ethyl acrylate, butadiene-acrylonitrile, butadiene-methacrylonitrile, butadiene-butene-1, butadiene-isobutene, isoprene-acrylonitrile, isoprene-methacrylonitrile, isoprene-butene-1, and isoprene-isobutene mixtures.<sup>(379–381,383,389)</sup> Cocatalyst combinations of triethylaluminum with trichloroacetic acid<sup>(385)</sup> and triisobutylaluminum with cobalt (III) acetylacetonate<sup>(388)</sup> have also been discovered to copolymerize MA with  $\alpha$ -olefins, cyclic olefins, and dienes. The triisobutylaluminum-cobalt (III) acetylacetonate catalyst is useful for producing alternating diene-MA copolymers. Boron fluoride will also copolymerize MA with dienes to give liquid resins.<sup>(382)</sup> The polymeric materials produced in these studies have not been characterized. However, patents claim these copolymers containing MA residues exhibit properties useful in adhesive and plastic applications. These systems have not had sufficient study to understand the role of MA in the catalyst systems and adequately describe the structure/property relationship of the obtained polymers.

A Ziegler catalyst system composed of diethylaluminum chloride and titanium chloride in toluene at  $0^\circ\text{C}$  has also been claimed useful for preparing vinyl ether–MA copolymers.<sup>(511)</sup> In typical experiments, the reactions were terminated after 3 h by adding methyl alcohol, and the product was purified by precipitation with excess alcohol. The yields vary with proportion of comonomers, 98% for a 7 : 1 mole fraction of isobutyl vinyl ether–MA, 92% for a 2–4 : 1 mole fraction, but only 44% for a 1 : 1.2 mole fraction. Similar



to the previous Ziegler catalysis work, the copolymers were not well characterized.

### 9.2.12. Vinyl Ketones

Solution copolymerization of methyl and phenyl vinyl ketones with MA, using free-radical initiators, gives good to fair yields of nonequimolar copolymers.<sup>(391,392)</sup>

The vinyl ketone copolymerizations were run in benzene or xylene at 50–135°C, using BPO initiator. Conversions were in the range 14–44% and increased as the temperature increased. The best yields of copolymer were obtained with phenyl vinyl ketone. Using feeds of 50–90 mol % anhydride, the copolymers contained 11–36 mol % anhydride. Solutions of the copolymers were generally highly colored. For example, *N,N*-dimethylformamide solutions were yellow-green, exhibiting a strong green fluorescence. The phenyl vinyl ketone copolymer, with a 64 : 36 molar ratio of ketone : anhydride, exhibited a polymer melt temperature (pmt) of 155–168°C. In comparison, the 73 : 27 methyl vinyl ketone : maleic anhydride copolymer exhibited a pmt of 171–176°C.

### 9.2.13. Carbon Monoxide

The patent literature describes a procedure for the copolymerization of MA with carbon monoxide.<sup>(509)</sup> Copolymerization is achieved in benzene solvent under a CO–N<sub>2</sub> mixed atmosphere at 600–700 psi and 100–110°C, with BPO initiator. The base-hydrolyzed copolymer greatly improved the detergent action of Sulframin 85, Na dodecylbenzenesulfonate detergent.

## 9.3. COPOLYMER ANALYSIS

Gross aspects of the MA copolymers may be analyzed by infrared or nuclear magnetic resonance (NMR) spectroscopy.<sup>(393,394)</sup> The methods are not limited by the type of comonomer. The integral absorptivity in the infrared curve is measured in two regions, at 5.2–5.6  $\mu$  (1 923–1 770  $\text{cm}^{-1}$ ) for anhydride and 5.6–6.00  $\mu$  (1 770–1 665  $\text{cm}^{-1}$ ) for ester and carboxyl. Half-esters and diesters also show bands at 8.0–8.5  $\mu$  (1 250–1 176  $\text{cm}^{-1}$ ), which are distinguished from the acids absorbing at 10.6  $\mu$  (940  $\text{cm}^{-1}$ ). The NMR spectra show shifts for the hydrogens in the anhydride ring at 3.25 ppm, but at 2.8 ppm after ring opening. Ester and carboxyl group protons are also easily identified.

Treatment of copolymers with excess butyl amine in polar solvents, mixing with acetic acid in dioxane, and detecting the amount of unreacted amine by

potentiometric titration with  $\text{HClO}_4$  in acetic acid provides an excellent method to determine anhydride content.<sup>(487)</sup> An error limit of  $\pm 0.5\%$  is achievable. Potentiometric titration techniques also provide an excellent technique for detecting the content of anhydride-containing copolymers in the presence of other polymeric materials<sup>(488)</sup> and for detecting free MA in the presence of MA-containing copolymers.<sup>(525)</sup>

## 9.4. TERPOLYMERIZATIONS, MONOMERS STUDIED

In relation to the practical interest of synthesizing copolymers of homogeneous composition, a number of studies has been devoted to the problem of azeotropy, i.e., the possibility of preparing a copolymer whose composition is exactly the same as that of the initial monomer feed mixture. In such a case the monomer feed and copolymer composition would remain constant as the reaction proceeds. For most binary compositions, where MA is not involved, this problem is often simply solved. However, the problem of being able to prepare MA copolymers of compositions equal to feed mixtures is well known; i.e., MA homopolymerizes with difficulty and copolymerizes with many electron-donating monomers to give only equimolar copolymers. Furthermore, this problem is compounded in MA copolymerizations with two or more monomers (see Chapter 10).<sup>(4,395)</sup> Nevertheless, MA has been copolymerized with a wide variety of two or more monomers to obtain polymeric materials that are potentially useful in many areas. We briefly review these copolymerizations and provide a MA terpolymerization patent listing (Table A.1).

### 9.4.1. Styrene Containing Terpolymers

The styrene-MA monomer pair has been combined with a variety of other vinyl monomers, including divinylbenzene,<sup>(396,397)</sup> vinyl acetate<sup>(395,398,400)</sup> acrylonitrile and methacrylonitrile,<sup>(376,395,399,408)</sup> vinyl ethers,<sup>(401,402)</sup> methacrylic esters,<sup>(395,404-409)</sup> acrylic acid,<sup>(395)</sup> and acrylic esters<sup>(410,411)</sup> and copolymerizations run in solution with free-radical initiators. The  $\alpha$ -methylstyrene-MA pair has also been copolymerized with acrylonitrile.<sup>(412)</sup>

In terpolymerizations with MA, where two azeotropic copolymer pairs can be formed, Slocombe<sup>(395)</sup> described an "azeotropic copolymer index." In the method, the monomer-terpolymer composition plots take the form of a triangular coordinate graph. A line connecting the points that represented the composition along the azeotropic line have unique properties, i.e., give clear terpolymers, whereas compositions removed from the line gave increasingly turbid polymers as their distance from the azeotropic line increased.



Such efforts to refine concepts dealing with predicting homogeneous terpolymerizations have continued.<sup>(4,413)</sup>

Jenner and Kellou<sup>(526)</sup> recently studied the pressure effect on azeotropy in free-radical terpolymerization of MA with acrylonitrile, diethyl fumarate, methyl acrylate, methyl methacrylate, methyl vinyl ketone, vinylidene chloride, norbornene,  $\alpha$ -methylstyrene, indene, and vinyl acetate, with styrene as the second comonomer common in all cases. It was found that ternary azeotropes were only possible for those systems where the first comonomers had positive  $e$  values, i.e., diethyl fumarate, acrylonitrile, methyl acrylate, methyl methacrylate, methyl vinyl ketone, and vinylidene chloride. Surprisingly, the coordinates of the ternary azeotropes were very little affected by variations of the pressure from 1–3,000 bars. Since reactivity ratios in multi-component polymerizations are sensitive to pressure, causing terpolymer composition to also be pressure dependent, a shift of the ternary azeotropic point would be expected. Why this occurs awaits further clarification.

Styrene–MA–divinylbenzene terpolymers have been prepared in kerosene,<sup>(414)</sup> aromatic naphtha,<sup>(415)</sup> dioxane,<sup>(416)</sup> and benzene.<sup>(417)</sup> The terpolymers have also been prepared in benzene/methyl alcohol mixtures at 100°C, with BPO initiator.<sup>(396)</sup> The fine powdery terpolymers are easily dispersed in poly(propylene), functioning both as a modifier and dye-assist agent. These products are also proposed as ion-exchange resins, membranes, and absorbents. Attempts to prepare the terpolymer from styrene, divinylbenzene, and monomethyl maleate failed to work as well, due to different copolymerization reactivity ratios.<sup>(1)</sup> Addition of a small amount of 2-vinylpyridine to the styrene–MA–divinylbenzene termonomer mixture provided improved ion-exchange resins.<sup>(397)</sup> The exchange capacity, i.e., metal-ion selectivity, was demonstrated and compared for a number of cations, including  $\text{Fe}^{3+}$ ,  $\text{U}^{4+}$ ,  $\text{Bi}^{3+}$ ,  $\text{Al}^{3+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Na}^+$ , and  $\text{K}^+$ .<sup>(352)</sup>

Copolymers of styrene–MA–divinylbenzene have been modified to include ethyl acrylate. Typically, mixtures of the four monomers were polymerized in a casting mold with BPO at 72–75°C.<sup>(418)</sup> The resulting sheet was heated in aqueous sodium hydroxide at 90–100°C until maximum swelling occurred. This gave a pliable, transparent sheet which could be used as an ion-permselective membrane in cells for the electrolysis of brines.

Styrene–MA–vinyl acetate terpolymers have been prepared and briefly examined as adhesive layers for polyester supports.<sup>(400)</sup> When compounded with other additives, materials of this type are useful adhesives in the subbing layer of photographic films.

A styrene–MA macroradical, i.e., growing polymeric radical, is easily prepared in benzene at 50°C using AIBN initiator.<sup>(399,408)</sup> Unique block copolymers can be prepared by combination of this macroradical with a third monomer, such as methyl methacrylate or acrylonitrile. A film of this type block copolymer consisting of styrene–methyl methacrylate–MA, may be



crosslinked with diamines and used as a separator material for sterilizable silver oxide–zinc cells.<sup>(404,405)</sup> Styrene–acrylonitrile (SAN) copolymer modified with 7–15 parts/weight MA has recently been shown to be useful for acrylonitrile–butadiene–styrene (ABS) graft copolymer modification, to give thermoplastic molding compounds with improved properties.<sup>(406)</sup> In particular, use of the terpolymer containing 7.5–15 parts raises the heat stability  $>12^{\circ}\text{C}$ . The compositions also have improved flame resistance, tenacity, tear-strength, weatherability, and workability. Chances are good this patent will be exercised to prepare commercial products. Copolymerization of the styrene–MA pair with various  $\alpha$ -olefins, such as isobutylene, propylene, and diisobutylene, in the presence of a rubbery polymer is also claimed to be useful for preparing improved thermoplastics.<sup>(407)</sup> These compositions also have improved heat resistance and impact resistance, along with being easily thermoformed into pipes, sheets, films, and bottles, e.g., by extrusion, milling, moulding, drawing, and blowing. This patent<sup>(407)</sup> is attractive for commercial practice.

Copolymerization of the styrene–MA pair with both acrylonitrile and vinylidene chloride has been explored for preparing coatings and adhesives.<sup>(376)</sup> A copolymer containing the four monomers in a 60.56:27.7:4.7:6.97 weight ratio with intrinsic viscosity of 0.83 dl/g and m.p. of  $172\text{--}80^{\circ}\text{C}$  was resistant to acids, many organic solvents, weathering, and temperatures  $\leq 120^{\circ}\text{C}$ . The copolymer exhibited good adhesion in bonding steel to steel, steel to stone, steel to glass, ceramic to stone, and glass to glass better than common epoxy resin adhesives.

Styrene-ethyl acrylate–MA terpolymers, prepared in toluene/*n*-butanol solvent mixtures with free-radical initiators can be used to prepare thermosetting acrylic coatings with high adhesion and gloss, good solvent resistance and weatherability.<sup>(411)</sup> The  $K$  and  $\alpha$  values in the Mark–Houwink–Sakurada equation, for viscometric determination of the terpolymer molecular weights in dioxane, were 0.603 and  $88.67 \times 10^{-3}$ , respectively.<sup>(410)</sup> Using a different procedure, styrene-ethyl acrylate–MA (40–70:20–50:10–20) terpolymer was produced in Solvesso 100 with di-*tert*-butyl peroxide at  $140\text{--}150^{\circ}\text{C}$ . After the polymerization was complete, 2-ethylhexanol was added to provide monoalkyl maleate residues. Materials of this nature may be formulated with epoxy resins, pigments, and amine catalysts and heat cured (crosslinked) to form chemically resistant, decorative metal coatings.<sup>(419)</sup> Other variations of this theme have also been explored for coatings.<sup>(420–422,489)</sup>

Mixtures of styrene–MA–glycidyl isopropenylphenyl ether, when copolymerized with radical initiators, give thermosetting resins in high yields.<sup>(402)</sup> Coatings formulated from these resins exhibit good gloss, adhesion, solvent resistance, and impact properties.

Combinations of bisphenol A diglycidyl ether diacrylate with the styrene and cobalt 2-ethyl hexanoate peroxide catalyst system are very rapidly cured at room temperature upon addition of small amounts of MA.<sup>(403)</sup> MA triggers

decomposition of the catalyst system to give free radicals for copolymerization initiation. No doubt MA copolymerization occurs in the process.

Copolymerizing the styrene-MA monomer pair with various organometallic monomers, such as trimethyl, triethyl, or tributylmethacryloxystannane or vinyltriethoxysilane, in benzene at 60°C with BPO, provides unique bacterial- and fungicidal-resistant copolymers.<sup>(409,423)</sup> Introduction of the Si, Sn, or Pb atoms in the terpolymers also improves the adhesion, lightfastness, thermal stability, and other properties of the materials.

#### 9.4.2. $\alpha$ -Olefin Containing Terpolymers

High-molecular-weight ( $10^6$ ) ethylene-co-MA-co-vinyl crotonate polymers have been described in the literature and given the name Malethamer resin in Europe.<sup>(424,425)</sup> The physicochemical properties of the terpolymers include inhibition of the growth of a wide variety of bacterial species *in vitro*. This suggests that this polymer could be used in treatment of infection in the alimentary canal. Dangerous side reactions may be eliminated in such an application, since the polymer may not be absorbed by the system.

Terpolymers of ethylene, MA, and diolefins have been obtained by solution polymerization in benzene.<sup>(426,427)</sup> The molecular weights of the copolymers increase with increasing proportion of diolefin, and insoluble gel formed at sufficiently high levels of the latter. The typical crosslinking monomers were hexadiene, diallyl ether, and the allyl esters of  $\alpha,\beta$ -unsaturated acids.

There are claims that terpolymers of ethylene, propylene, and MA (mol % 47:50:3) can be produced by a continuous process in hexane solution with a modified Ziegler catalyst (ethyl aluminum dichloride-vanadyl trichloride).<sup>(379)</sup> For the procedure, a carbon tetrachloride solution of the anhydride was added to the reaction mixture after copolymerization of the olefin mixture was well established. The copolymers, obtained by this technique as sticky glasses, have not had adequate study. Also fundamentals of the polymerization reaction have not been explored.

#### 9.4.3. Vinyl Acetate Containing Terpolymers

In addition to the terpolymers previously mentioned in Sec. 9.4.1, the vinyl acetate-MA monomer pair has also been copolymerized with diethyl fumarate,<sup>(394)</sup> lauryl fumarate,<sup>(429-433)</sup> allyl acetate,<sup>(394)</sup> vinyl crotonate,<sup>(434)</sup> and vinyl chloride.<sup>(394,435-442)</sup>

The incorporation of small amounts of MA or maleic acid into vinyl chloride-vinyl acetate copolymers substantially improves their stability and adhesion.<sup>(439)</sup> The introduction of the anhydride group also significantly increases the viscosity of the copolymers. Terpolymers of this type, having a



vinyl chloride–vinyl acetate–MA composition of 85–88 : 11 : 1–3 (mol %), are commercial, being marketed for metal coating applications.

The vinyl chloride–vinyl acetate–MA terpolymers are conveniently made in acetone, with acetyl peroxide initiator.<sup>(443)</sup> Suspension polymerization techniques are used to prepare the terpolymer as a fine powder.<sup>(437,444)</sup> A recent example of this procedure employs a protective colloid, potassium persulfate initiator, and trichloroethylene chain regulator.<sup>(437)</sup> Terpolymers of this type exhibit good solubility in ketone solvents. Applications claimed for the terpolymer include adhesives for metals and textiles,<sup>(235,435,436,438)</sup> decorative metal coatings,<sup>(440–442)</sup> heat sealable adhesives for packaging films,<sup>(445,446)</sup> printing inks,<sup>(447)</sup> can coatings,<sup>(448–450)</sup> vinyl plastisol coatings for steel,<sup>(451)</sup> binders for electrophotographic coatings for paper,<sup>(452)</sup> and glossy paper coatings.<sup>(453)</sup>

Interpolymerizing vinyl acetate, acrylic acid, and a monoalkyl ester of maleic or fumaric acid, in which the alkyl group contains 1–8 carbon atoms, gives materials used for sizing spun polyester or polyester blends.<sup>(480)</sup> The formulations contained about 2% by weight of the maleate.

Vinyl acetate terpolymers prepared with lauryl fumarate are claimed useful as ashless detergency additives, viscosity index improvers, dispersants, etc., for lubricating oils<sup>(429,431,432)</sup> and additives to improve jet fuel lubricity.<sup>(433)</sup> At one time, the copolymerization of the vinyl acetate–diethyl fumarate pair with ethylene was explored as a procedure for preparing plastics.<sup>(502)</sup> The hydrolyzed interpolymers crosslinked on heating at 150°C to give moldings. The patent literature also discloses that vinyl acetate terpolymers containing di(2-ethylhexyl)maleate and 2-ethylhexyl acrylate exhibit characteristics useful as pressure-sensitive adhesives.<sup>(428)</sup>

#### 9.4.4. Acrylate and Methacrylate Containing Terpolymers

In addition to the terpolymers previously mentioned that contain acrylates,<sup>(395,404–409)</sup> the methyl acrylate–MA and methyl methacrylate–MA monomer pairs have been copolymerized with each other,<sup>(454)</sup> acrylic acid,<sup>(395)</sup> 2-ethylhexyl acrylate,<sup>(420)</sup> ethyl acrylate,<sup>(455)</sup> glycidyl methacrylate,<sup>(456)</sup> acrylonitrile,<sup>(457,458)</sup> vinylidene chloride,<sup>(443,459)</sup> and isobutyl vinyl ether.<sup>(460)</sup>

Compositional determinations for the methyl methacrylate–MA–methyl acrylate terpolymers, prepared with BPO in 2-butanone solvent at 60°C, showed the reactivity of the methacrylate monomer toward the anhydride macroradical is approximately four times greater than that of the acrylate.<sup>(454)</sup> Even though evidence for charge-transfer complexes between the anhydride–acrylate and anhydride–methacrylate pairs exist (see Chapter 10), there is no evidence that the kinetics of the polymerization is affected by these complexes.<sup>(454)</sup>

The copolymerization of isobutyl vinyl ether–MA–methyl methacrylate monomer mixtures were run in sealed tubes at 60°C, with AIBN initiator and



ethyl acetate solvent. The rates of polymerization of the individual monomers were followed by NMR. From the data obtained, it was concluded that the polymer formed from the mixture of the three monomers was a block copolymer made up of methacrylate and anhydride–vinyl ether units, where the length of each unit depended on the monomer feed concentrations. It could be observed that the methacrylate polymerized at essentially the same rate in all experiments, regardless of the presence of the other monomers. Since it is well known that vinyl ether–MA pairs very readily undergo free-radical-initiated alternating polymerization (see Chapter 10), the results of the study are predictable.<sup>(460)</sup>

Terpolymers, prepared from various methacrylate–MA pairs, copolymerization with glycidyl methacrylate and acrylonitrile have been examined in water-soluble films and coatings<sup>(456)</sup> and wood–plastic combinations.<sup>(457,458)</sup> The thermosetting coatings exhibited excellent protective and decorative properties. Wood–plastic combinations prepared by this procedure exhibited excellent dimensional stability and other properties, due to significant condensation reaction of the anhydride groups with cellulosic hydroxyl residues.

Copolymers of 2-ethylhexyl acrylate, vinyl acetate, and MA, in the range 59–64 : 35–40 : 1, have been produced in isopropyl acetate or dichloromethane solvents.<sup>(461)</sup> Formulation of the materials with epoxy plasticizers, solution applied and cured 3 min at 275°F on poly(vinyl chloride) gave excellent pressure-sensitive adhesive films. The small amount of anhydride lowered both shrinkage and improved the cohesion of the applied films. A version of the same theme, i.e., solution copolymerization of octyl acrylate, ethyl acrylate, vinyl acetate, and MA (70 : 10 : 20 : 7.5) also provides useful pressure-sensitive adhesives.<sup>(462)</sup> A recent patent<sup>(483)</sup> also shows that copolymerization of aqueous dispersions of VA, 2-ethylhexyl acrylate, bis(2-ethylhexyl) maleate, and ethylene in various ratios provides a technique for obtaining pressure-sensitive adhesives exhibiting high tack and excellent adhesion to various surfaces.

Long-chain alkyl methacrylates, ethyl acrylate, and a small amount of MA have been copolymerized in high boiling naptha with peroxides and promoters such as Hyamine 22 (quaternary ammonium salt) at 105°C. The solutions have been used as a modifier for baking enamels.<sup>(463)</sup> Post reaction of the anhydride moiety in the terpolymer with aminoethyl ethylene urea formed detergent additives for fuel and lube oils.<sup>(464)</sup>

The potassium, ammonium, or amine salts of interpolymers prepared from monomers such as lauryl methacrylate, methyl methacrylate, and maleic acid are of particular utility in the disposable nonwoven industry where there is need for polymers that will absorb and retain water and ionic physiological fluids.<sup>(481)</sup> In general, the polymeric coatings give a durable, antistatic, antisoilable finish to a variety of filamentary materials.

Methyl methacrylate–ethyl acrylate–MA mixtures have been combined with degraded crepe rubber (2% on monomers), BPO, and hydrocarbon solvents and polymerizations run at 75°C. The products, which were obtained as fine dispersions, could be cured on glass at 150°C to obtain coatings with excellent adhesion.<sup>(465)</sup>

Methyl methacrylate-2-ethylhexyl acrylate–MA terpolymers, in the compositional range 40–50 : 42–52 : 8, have been prepared in naptha at 130–140°C to obtain coating resins.<sup>(420)</sup> Postreaction of the materials with trimethylolpropane, which introduced both hydroxyl and carboxyl sites on the terpolymer backbone, provided reactive moieties for amino-resin crosslinkers. Unsaturated monohydroxy dialkyl maleates and fumarates, such as 2-hydroxyethyl isobutyl fumarate, have also been copolymerized with various acrylate–methacrylate combinations to obtain low-viscosity, heat-hardening, film-forming copolymers.<sup>(492)</sup> These copolymers may also be crosslinked with amino resins to provide valuable protective coating.

#### 9.4.5. Miscellaneous Terpolymers

Maleic anhydride has also been free-radical copolymerized with a number of other monomer pairs, such as allyl acetate–allyl chloride,<sup>(395)</sup> vinyl chloride–diethyl fumarate,<sup>(395)</sup> acrylamide–methacrylic acid,<sup>(468,469)</sup> trimethylolpropane allyl ethers–methyl acrylate,<sup>(466)</sup> and styrene–acetyltriethyl citrate.<sup>(467)</sup> Systems of this type are very briefly reviewed.

Using a water-in-oil dispersion process, water-soluble copolymers of acrylamide, methacrylic acid, and MA (85–90 : 4–9 : 0.5–1) were prepared as white granular solids.<sup>(468)</sup> An aqueous solution of the monomers, at pH 9, was added to toluene at 70°C with persulfate/bisulfite redox initiator. The system was sparged continuously with nitrogen during polymerization. Azeotropic distillation of the water left a slurry from which the product was collected by filtration. The terpolymers were shown to be effective flocculants for paper-pulp slurries and retention aids for the deposition of fillers in papers.<sup>(469)</sup> The materials have been approved for modification of paper and paperboard used in packaging food.<sup>(470)</sup>

The allyl ether based terpolymers were prepared and investigated as surface coatings.<sup>(466)</sup> Copolymerization of the acetyltriethyl citrate–styrene–MA mixtures on glass cloth, with peroxide initiators, was shown to be useful for preparing glass laminates.<sup>(467)</sup> Diallyl fumarate–allyl chloride copolymerizations with styrene has been explored as a technique to prepare thermosetting resins.<sup>(504)</sup> The soluble fusible resins could be cured at elevated temperatures to give coatings and plastics.

Phenyl dichlorophosphine is known to undergo free-radical-initiated copolymerization with styrene. When MA is added to the mixture, the propagation rate is enhanced, generating terpolymers containing MA.<sup>(471,472)</sup>



A 5.5-fold increase in rate of copolymerization was observed for the system, using only 1 mol % anhydride. Charge-transfer complex formation between AIBN initiator and MA was postulated to play a role in the observed rate acceleration.

## 9.5. COPOLYMER USES

In addition to the previously mentioned articles and patents that disclose possible uses of copolymers and terpolymers containing MA, many additional patents (Table A.1) also describe other compositions and uses for terpolymers with MA residues. As shown in Table A.1 terpolymer compositions have also been prepared, with possible uses including molding resins, coatings, adhesives, structural foams, laminates, printing inks, paper and textile sizes, lubricating and fuel oil additives, thickening agents, detergent additives, cation-exchange resins, synthetic paper, polymeric emulsifiers, clay beneficiation agents, flocculants, enzyme and medicinal carriers, paper wet-strength additives, epoxy resin hardener, packaging films, membranes, and a number of other applications.

## 9.6. EPILOGUE

The great amount of work on copolymers containing MA residues or monomer residues derived from MA, coupled with the many possible uses for such materials, has failed to produce anything resembling a commensurate market for MA. This could change as greater recognition is given to the great versatility of MA for the production of copolymers containing anhydride, acid, ester, amide, and imide groups and the attendant properties these groups confer on polymers. The chemistry is there and the economics competitive.

## APPENDIX TO CHAPTER 9

Maleic Anhydride ( $M_1$ )– $M_2$  Reactivity Ratios<sup>a</sup>

$M_2$	$r_1$	+ / –	$r_2$	+ / –	Temperature (°C)	References
Acenaphthylene	0.07	0.03	0.43	0.04	60 <sup>b</sup>	12
	0.10	0.05	0.32	0.10	60 <sup>b</sup>	12
Acetylene, phenyl	0.065	0.005	0.076	0.006	—	13
Acrolein, diethyl	0.2	—	0	—	—	14
acetal	0.18	0.04	0.07	0.01	—	15



Maleic Anhydride (M<sub>1</sub>)–M<sub>2</sub>) Reactivity Ratios<sup>a</sup> (cont.)

M <sub>2</sub>	r <sub>1</sub>	+ / –	r <sub>2</sub>	+ / –	Temperature (°C)	References
Acetic acid, allyl ester	0.13 <sup>d</sup>	—	0.007 <sup>d</sup>	—	30	16
	0.018	—	0.005	—	—	16
	0.018	—	0.030	—	60	18
Acetic acid, vinyl ester	0.072	0.04	0.01	—	—	107
	0.055 <sup>d</sup>	0.015	0.003 <sup>d</sup>	—	75	17
Acetic acid, isopropenyl ester	0.002	—	0.032	0.005	75	17
Acrylamide	0	—	0.75	—	50	19
	0.3	—	0.25	—	70	19
Acrylic acid, 2-chloroethyl ester	0.03	0.05	6.2	0.5	60	20
Acrylic acid, methyl ester	0	—	2.50	—	60	21
	0.02 <sup>d</sup>	—	2.80 <sup>d</sup>	0.05	75	17
	0.007	—	2.15	—	50	22
	0.008	—	2.50	—	70	22
Acrylic acid, ferro cenylmethyl ester	0.11	—	0.61	—	—	23
Acrylic acid, tetra hydrofurfuryl ester	0.03	—	1.65	—	70	24
	0	—	1.25	—	30	24
Acrylonitrile	0	—	6	—	60	21
	0	—	7.7	0.3	—	25
Allylidene, diacetate	0.5	—	0	—	—	14
Benzoic acid, β-vinyl oxyethyl (3,5-di-tert-butyl-4-hydroxy) ester	0	—	0	—	—	26
Butadiene, 2,3-dimethyl	– 0.021	0.038	– 0.037	0.059	—	26, 27
Butadiene, 2,3-bis (diethyl phosphono)	0.07	0.02	0.15	0.03	—	28
	0.07	0.03	0.17	0.03	—	28
	0.30	0.12	0.12	0.08	—	28
2-Butene, cis-	0.016	0.005	0	—	60	29a
	0.016	0.005	0	—	60	29b
2-Butene, trans-	0.030	0.009	0	—	60	29a
	0.030	0.009	0	—	60	29b
2-Butene, 2-methyl	0.005	0.002	0	—	60	29b
	0.010 <sup>c</sup>	—	0.035	—	70	430
Caprolactam, N-vinyl	0.17	—	0.006	—	70	31
Carbamic acid, N,N-diethyl, o-vinyl ester	0	—	0.035	—	80	32
Cinnamic acid, vinyl-oxyethyl ester	0.14	—	0.21	—	—	33
Crotonaldehyde, diethylacetal	8.5	—	0.01	—	—	34
Crotononitrile, cis-	0	—	0	—	60	29b
Cyanoacetic acid, a,α-diallyl, ethyl ester	1.4	—	0.04	—	—	35

Maleic Anhydride (M<sub>1</sub>)–M<sub>2</sub> Reactivity Ratios<sup>a</sup> (cont.)

M <sub>2</sub>	r <sub>1</sub>	+ / –	r <sub>2</sub>	+ / –	Temperature (°C)	References
Cycloheptene	0.068	0.002	0	—	60	29a
Cyclohexane, vinyl	0.22	—	0.008	—	65	36
Cyclohexane, 4-vinyl epoxy	0.14	—	0.004	—	—	37
Cyclohexene	0.083	0.005	0	—	60	29
Cyclohexene, 4-cyano-	0.070	—	0.388	—	—	38
Cyclooctene	0.067	0.006	0	—	60	29a
Cyclopentene	0.010	0.003	0	—	60	29a
	0.49 <sup>a</sup>	—	0.049	—	—	108
	0.21 <sup>a</sup>		0.041			108
	0.10 <sup>a</sup>		0.030			108
Cyclopropane, 1,1- dichloro-2-vinyl	0.41	—	0.10	—	—	39
2,3-Dihydropyran	0.006 5	0.002 3	–0.056	0.059	60	40
1,3-Dioxane, 2-iso propenyl	0.037	—	0.081	—	—	41
1,3-Dioxane, 2-iso propenyl-4-methyl	0.004	—	0.009	—	—	41
1,3-Dioxane, 2-isopro propenyl-5,5-dimethyl	0.01	—	0.001 4	—	—	41
1,3-Dioxane, 2-styryl- 4-methyl	0.09	—	0.09	—	—	41
1,3-Dioxene-4,4-methyl	0.18	—	0	—	50	42
1,3-Dioxolane, 2-vinyl-	0.17	—	0.12	—	60	43
1,3-Dithiolane	0.61	—	0.60	—	40	473
	0.72	—	1.40	—	40	473
Ether, allyl glycidyl	0.002	—	0.01	—	60	44, 49
Ether, butyl vinyl	0.045	—	0	—	50	45
	0	0.01	0	0.004	—	46
Ether, 2-chloroethyl vinyl	0.005	—	0.009	—	—	47
Ether, dodecyl vinyl	0.046	0.052	–0.046	0.054	50	48
Ether, glycidyl vinyl	0.031	—	0.104	—	—	49
Ether, ethylene glycol divinyl	0.01	0.003	0.14	0.037	—	50
Ether, hydroquinone divinyl	0.09	—	0.01	—	—	51
	0	0.07	0.165	0.06	—	50
Ethylene	0	—	0	—	40	52
Ethylene, chloro-	0.008 <sup>d</sup>	—	0.296 <sup>d</sup>	0.07	75	17
	0.40	—	0.037	—	60	53
	0.668	—	0.104	—	60	53
Ethylene, 1,1-dichloro-	0	—	9	—	60	21
Ethylene, 1,1,2-tri chloro-	0	—	3.7	—	—	54

Maleic Anhydride (M<sub>1</sub>)-M<sub>2</sub> Reactivity Ratios<sup>a</sup> (cont.)

M <sub>2</sub>	r <sub>1</sub>	+ / -	r <sub>2</sub>	+ / -	Temperature (°C)	References
1-Hexene	0.15 <sup>b</sup>	—	0.015	—	70	430
2-Ethyl-1-hexene	0.15 <sup>b</sup>	—	0.015	—	70	430
Ketone, methyl 5-Norbornen-2-yl	0	—	0.4	—	60	55
Ketone, vinyl cyclohexyl	0.013	—	0.046	—	—	56
Malononitrile, methylene	0		45	—	50	57
Methacrylic acid, 2-Chloroethyl ester	0.003 4	0.0026	5.32	0.38	—	58
Methacrylic Acid, 2,3- epoxypropyl ester	0	—	4.5	—	40	59
	0	—	4.2	—	50	59
Methacrylic acid, ferro cenyl methyl Ester	0.10	—	0.28	—	—	23
Methacrylic acid, methyl ester	0.00	—	0.96	—	60	60
	0.01	—	0.50	—	60	60
	0.01	—	3.10	—	60	60
	0.01	—	3.85	—	60	60
	0.01	—	3.40	—	60	60
	0.02	—	3.85	—	60	60
	0.02	—	0.90	—	60	60
	0.02 <sup>d</sup>	—	6.7 <sup>d</sup>	0.2	75	17
	0.03 <sup>d</sup>	—	3.5	—	60	61
	0.50 <sup>d</sup>	0.3	1.0	0.4	30	62
	-0.18 <sup>d</sup>	0.28	4.63 <sup>d</sup>	1.14	30	63
	0	—	2.1	—	—	64
	0	—	2.4	—	—	64
Methacrylic acid, trimethylstannyl ester	0	—	0.220	—	—	65
	0	—	0.20	—	—	66
Methacrylic acid, triethyl stannyl ester	0	—	0.12	—	—	65
Methacrylic acid, tri- propyl stannyl ester	0	—	0.081	—	—	65
Methacrylic acid tri- butyl stannyl ester	0	—	0.053	—	—	65
Methacrylonitrile	-0.001 7	0.002 4	18.1	1.4	—	58
Naphthalene, 1,2-di	0.026	—	0	—	60	67
hydro-	0.28	—	0	—	60	67
Naphthalene, 2-isopro- penyl-	0.09	—	0	—	60	68
Norbornene	0.03 <sup>b</sup>	—	0.05	—	70	430
5-Norbornene-2-acetyl	0.4	—	0	—	60	55
5-Norbornene-2-	0.012	—	0.16	—	—	55
carbonitrile	0.12	—	0.04	—	—	69, 70



Maleic Anhydride (M<sub>1</sub>)–M<sub>2</sub> Reactivity Ratios<sup>a</sup> (cont.)

M <sub>2</sub>	<i>r</i> <sub>1</sub>	+ / –	<i>r</i> <sub>2</sub>	+ / –	Temperature (°C)	References
5-Norbornene-2-carboxylic acid	0.07 0.03 0.36	—	17.3 12.35 0.08	— — —	— — —	71, 74 72, 73 70
5-Norbornene-2-carboxylic acid, methyl ester	0 0.26	— —	1.1 0.10	— —	60 —	54 69, 70
5-Norbornene-2-carboxylic acid, 2-methyl-, methyl ester	0	—	1.1	—	60	54
Pentaerythritol, diallylidene	0.03	—	0.08	—	—	75
Pentaerythritol, dicrotylidene	0.02	—	0.02	—	—	76
Pentaerythritol, dimethyl allylidene	0.050	—	0.025	—	—	76
Phthalic acid, diallyl ester	0.06	—	0.015	—	—	35
Phthalimide, <i>N</i> -vinyl	0.001 0.003 0.84 0.014	— — — —	0.20 0.30 0.20 0.20	— — — —	65 90 — —	77 78 79, 80 81
1-Propene, 1-chloro- <i>cis</i> -	0.41	—	0.004	—	60	82
1-Propene, 1-chloro- <i>trans</i>	0.26	—	0.05	—	60	82
1-Propene, 2-chloro-	0.06	—	0.06	—	60	82, 83
1-Propene, 3-chloro-	0.19	0.18	–0.03	0.11	—	84
1-Propene, 3-chloro-2-methyl	—	—	0.18	0.05	155	85
2-Propen-1-ol, 2-chloro-acetate	0	—	0		120	86
Pyridazinone, 6-methyl, 3-(2-vinyl)-	0.01	—	0.10	—	—	87
Pyridinium, 1,2-dimethyl-5-vinyl methyl sulfate	0.06		12.04	—	55	88
2-Pyrrolidinone, 1-vinyl	0.074	0.04	–0.027	0.02	30	89
Silane, triethoxy vinyl-	0.035	—	0.004	—	70	90
Stilbene, <i>cis</i>	0.08	0.08	0.07	0.07	60	91
Stilbene, <i>trans</i>	0.03 0.13 0.03	0.03 0.02 0.01	0.03 0 0	0.03 — —	60 70 60	91 92 92
Styrene	0 0 <sup>d</sup>	— —	0.04 0.019	0.006 —	— 50	17 93

Maleic Anhydride (M<sub>1</sub>)–M<sub>2</sub> Reactivity Ratios<sup>a</sup> (*cont.*)

M <sub>2</sub>	<i>r</i> <sub>1</sub>	+ / –	<i>r</i> <sub>2</sub>	+ / –	Temperature (°C)	References
Styrene	0	—	0.02	—	60	94
	0	—	0.02	—	60	95
	0	—	0.01	—	60	21
	0 <sup>d</sup>	—	0.042 <sup>d</sup>	0.008	80	96
	0.002 <sup>d</sup>	0.002	0.097 <sup>d</sup>	0.002	50	97
	0.001	0.001	0.035	0.003	70	98
	0.005	0.001	0.13	0.03	70	98
	0.005	0.001	0.050	0.005	70	98
	0.01	—	0.041	—	60	99
	0.010	0.002	0.025	0.005	70	98
	0.015	—	0.040	—	50	100
	0.018	0.001	0.043	0.005	70	98
	0.035 <sup>d</sup>	0.002	0.012 <sup>d</sup>	0.009	40	101
	0.049	0.005	0.040	0.005	70	98
	0.001	—	0.025	—	—	102
	0.049	—	0.13	—	—	102
	0	—	0.02	—	—	103
	0.27	0.03	0.005	0.005	60	104
	0.08	0.03	0.038	0.003	60	104
	0.005 <sup>c</sup>	—	0.040	—	70	430
Succinimide, <i>N</i> -vinyl-	0.03 <sup>d</sup>	—	0.15 <sup>d</sup>	—	60	78
Sulfide, isobutyl	0	—	0	—	—	105
vinyl						
Thiophene	0.020 <sup>c</sup>	—	0	—	70	430
Vinyl ferrocene	0.21	0.2	0.02	0.1	—	106
Vinylidene cyanide	0		45	—	—	3, 57

<sup>a</sup> Some of the *r*<sub>1</sub> and *r*<sub>2</sub> values should be used with caution, since it was difficult in some cases to assign claimed values. Also, no attempt was made to evaluate the experimental techniques or methods used to estimate the *r*<sub>1</sub> and *r*<sub>2</sub> values.<sup>(2,3)</sup>

<sup>b</sup> Copolymerizations run at 1.0, 2 000, and 4 000 kbars/cm<sup>2</sup> to get *r*<sub>1</sub> values, respectively of 0.49, 0.21, and 0.10.

<sup>c</sup> Reactivity ratios change slightly when copolymerizations run at 3 kbars.

<sup>d</sup> Greenly<sup>(527)</sup> recently recalculated these *r*<sub>1</sub> and *r*<sub>2</sub> values using the Kelen and Tudos<sup>(3)</sup> procedure.

Copolymerization Parameters

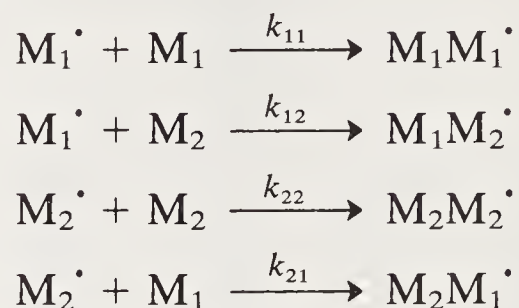
A. Reactivity Ratios

The copolymer equation has long been the foundation by which specific copolymer compositions could be designed.<sup>(1,7)</sup> When two monomers (M<sub>1</sub> and M<sub>2</sub>) copolymerize, the relationship between the composition of the copolymer and the composition of the monomer mixture is given by the following equation:

$$\frac{dm_1}{dm_2} = \frac{M_1(r_1M_1 + M_2)}{M_2(r_2M_2 + M_1)}$$

where  $M_1$  and  $M_2$  are moles of monomer 1 and monomer 2 in monomer mixture;  $m_1$  and  $m_2$  are moles of monomer 1 and monomer 2 entering the copolymer;  $r_1$  and  $r_2$  are the reactivity ratios for monomer 1 and monomer 2.

The chain-propagating reactions occurring when two monomers ( $M_1$  and  $M_2$ ) are present may be written as follows:



where  $M_1\cdot$  and  $M_2\cdot$  are polymer chains ending in a radical derived from monomer 1 and monomer 2.

The monomer reactivity ratios ( $r_1$  and  $r_2$ ), for any monomer pair, are defined as follows:

$$\begin{aligned} r_1 &= k_{11}/k_{12} \\ r_2 &= k_{22}/k_{21} \end{aligned}$$

The product of the polymerization constants,  $r_1r_2$ , is very frequently used as an index for evaluating the alternating tendency in binary copolymerization.<sup>(4,5)</sup> In fact, the reciprocal of the product  $r_1r_2$  is often called the alternation tendency index. The ideal (random) copolymerization condition exists for the case  $r_1r_2 = 1$ .<sup>(6)</sup> Where  $r_1$  and  $r_2$  are very low and the  $r_1r_2$  product tends to zero the alternating tendency increases.<sup>(4,5)</sup> The product  $r_1r_2$  can be zero in two cases—where one or both reactivity ratios are zero. Where  $r_1 = 0$ , the copolymer chain is built of isolated  $M_1$  units separated by sequences of  $M_2$  monomer units. Strictly alternating copolymer would be obtained when both  $r_1$  and  $r_2$  are zero. The second condition is often found for MA copolymerizations, as described in Chapter 10. Where  $r_1 > 1$ , the polymer is richer in  $M_1$  monomers than the monomer feed. For  $r_1 < 1$ , the opposite holds.

Monomer reactivity ratios, deduced from copolymerizations, have been widely used for comparison of the reactivities of monomers toward reference polymer radicals. The reader is cautioned that this procedure is unreliable for polymer radicals showing very low reactivities toward their monomers; this limitation applies to the MA polymer radical.

### B. *Q and e Values*

The reactivity ratios depend on the system used for their determination and must be determined for each monomer pair of interest. Alfrey and Price<sup>(8)</sup> recognized the need for general and constant parameters by which a given monomer could be characterized. This led to the development of the *Q-e*



scheme, i.e., the concept that reactivity ratios were a function of two fundamental parameters:  $Q$ , representing the resonance stabilization of monomers and its corresponding radical adduct in copolymerization, and  $e$ , representing the polarity of monomer and radical adduct in copolymerization. Accordingly,  $r_1$  and  $r_2$  may be defined as follows:

$$r_1 = k_{11}/k_{12} = (Q_1/Q_2)\exp[-e_1(e_1 - e_2)]$$

$$r_2 = k_{22}/k_{21} = (Q_2/Q_1)\exp[-e_2(e_2 - e_1)]$$

Since the  $Q$ - $e$  scheme is generally regarded as an empirical relationship, which does not adequately predict the copolymerization profile of many monomer pairs, many have expressed dissatisfaction with its use and determination.<sup>(9,10)</sup> However, it is still a useful tool for assessing the reactivity and possible copolymerization of untried monomer combinations in binary and multicomponent polymerization systems.<sup>(4,11)</sup>  $Q$  and  $e$  values that have been reported in the literature for MA, are listed as follows:

$Q$	$e$	Reference
0.23	2.25	1
0.51	3.17	10
0.18	2.65	17
0.86	3.69	528

By definition, styrene is given the values  $Q = 1$  and  $e = -0.80$ .<sup>(1)</sup> This being true, it is predictable that styrene and MA should readily copolymerize, as shown in Chapters 9 and 10. Many of the other monomers, such as olefins, vinyl ethers, vinyl esters, allyl monomers, and dienes also have negative  $e$  values, showing that they should also undergo facile copolymerization with MA (see Chapter 10).



# ALTERNATING ADDITION COPOLYMERIZATIONS

## 10.1. INTRODUCTION

Conventional free-radical-initiated copolymerizations usually result in random copolymers. At the same time, certain monomer pairs are known to copolymerize giving regular alternation products, regardless of the composition of the monomer mixture. Behavior of the second type is characteristic of monomers differing considerably in their electron donor–acceptor character. The latter knowledge brought about a great resurgence of interest in the study of free-radical-initiated copolymerizations and many of these studies were concerned with MA. This interest was further kindled by the suggestion that the alternating tendency in some copolymerizations could arise from the participation of a 1 : 1 monomer–monomer donor–acceptor or charge-transfer complex (CTC) in the propagation reaction. Prior to this suggestion, it had generally been assumed that any alternating tendency arose as a consequence of the inherent reactivities of the monomers and radicals involved. As mentioned in Chapter 9, reactivity concepts were rationalized in terms of resonance and polar effects in semiempirical schemes such as the  $Q-e$ <sup>(1)</sup> and “patterns”<sup>(2)</sup> concepts.

Even though MA will not easily homopolymerize (see Chapter 8), it is known to copolymerize readily with a variety of electron-donor monomers or monomers of opposite polarity to yield alternating copolymers. It is interesting to note that substituted maleic anhydrides, such as monophenyl, monomethyl, dimethyl, monochloro, monobromo, monofluoro, dichloro, and difluoro derivatives, even though studied very little (see Chapter 8), should also perform in some cases as electron-acceptor monomers and undergo alternating copolymerization with select donor monomers.<sup>(204,215,450,470,471,474,525,656,1024,1031,1051,1130)</sup> Imide derivatives of MA (see Chapter 8), such as *N*-phenylmaleimide<sup>(213,726)</sup> and various isomaleimides,<sup>(1032)</sup> as well as fumarates and mal-eates<sup>(85,140,176,400,534,537,541,544,558,831,893,1079)</sup> are known to have the tendency to undergo equimolar copolymerization with electron-donor monomers. It is also especially interesting that many 1,2-substituted and cyclic olefins, which will not undergo free-radical polymerization, will yield copolymers where MA is present. The copolymerization of *trans*-stilbene and MA, first reported in 1930, is one illustration of this behavior.<sup>(3)</sup> Much later, Bartlett and Nozaki<sup>(4)</sup>



discovered that the ratio of allyl acetate to MA in the copolymer of these two monomers, produced with radical initiators, was equimolar. This and other studies led these authors to be first to suggest the possibility that electron transfer from a donor radical to an acceptor monomer, or vice versa, in an activated CTC may account for the observed alternation tendencies.<sup>(4)</sup> Later, some authors supported this suggestion,<sup>(5-9,11,12)</sup> while others raised points of controversy.<sup>(13,14,17,18)</sup> With this stimulus and the desire to commercially exploit alternating copolymers, studies accelerated internationally on charge-transfer complexes and alternating copolymers. A large portion of the growing literature on this subject is concerned with copolymerization reactions in which MA is one of the two or more monomers entering into a CTC interaction.

The numerous investigations on allyl compounds, vinyl ethers, olefins, styrenes, divinyl monomers, etc., alternating copolymers with MA have led some to conclude that the mechanism of alternating copolymerization is too complex and cannot be understood on the basis of past concepts about radical reactivity. The most common view holds that the reaction occurs by preliminary formation of a CTC between the monomers<sup>(19-24)</sup> or a CTC between the propagating radical and the monomer.<sup>(25,26)</sup> Another view holds that these copolymerizations occur by successive combinations of monomers with greatly differing polarity.<sup>(27-29)</sup> These views, the large number of alternating MA copolymer systems, commercially available materials, applications, and so forth are reviewed in this chapter.

## 10.2. MONOMER PAIRS STUDIED

### 10.2.1. Allyl Monomers

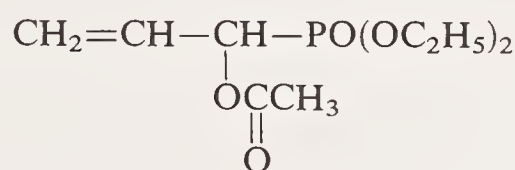
A large amount of an initiator is generally required to homopolymerize both allyl compounds and MA. In the process, only low-molecular-weight materials are obtained due to the high inclination of these monomers to engage in degradative chain-transfer processes. Thus, greatly enhanced interest in free-radical-initiated copolymerizations developed when it was discovered that relatively high molecular weight and good yields of copolymers could be formed from MA and several allyl compounds.

As previously mentioned, Bartlett and Nozaki<sup>(4)</sup> thoroughly studied the benzoyl peroxide (BPO) initiated copolymerization of allyl acetate with MA. They estimated that a 4.58-wt. % initiator concentration produced a copolymer of 36 600 kinetic chain length. Under comparable conditions, allyl acetate and MA gave very low-molecular-weight homopolymers. For the copolymerization, it was clearly established that the cross-propagation step is able to compete fairly effectively with allyl termination.

Allyl acetate–MA mixtures undergo rapid and highly selective copolymerization in the presence of peroxide initiators. For example, copolymerization is more rapid at 30°C than the homopolymerization of either monomer at 80°C. The copolymer prepared with 4.58 wt. % BPO shows limited solubility in all solvents except water and exhibits a molecular weight of approximately 40 000. The great propensity for 1 : 1 alternation cannot be correlated with any abnormal vapor pressures, solubilities, or viscosities of the monomer mixture.<sup>(4)</sup> However, alternating copolymerization would be expected with allyl acetate having  $Q = 0.028$  and  $e = -1.13$ .<sup>(41)</sup>

Using azobisisobutyronitrile (AIBN) initiator, benzene solvent, and a polymerization temperature of 60°C, others confirmed the alternation copolymerization of MA with allyl acetate.<sup>(30,33)</sup> Alternating copolymers were obtained with reduced viscosities of 0.11–0.19 dl/g, measured for 0.2% solutions of copolymer in *N,N*-dimethylformamide at 30°C. Equimolar allyl benzoate–MA copolymer, which has had very little study, may also be easily obtained with peroxide initiators.<sup>(1011)</sup>

A phosphonate derivative of allyl acetate, i.e., diethyl acetonylallylphosphonate (DEAP acetate) **1** behaves similar to allyl acetate



**1** DEAP acetate

when copolymerized with MA.<sup>(35)</sup> Various monomer mixtures (1 : 2, 1 : 1, and 2 : 1 molar ratios), when treated with AIBN initiator for 15 h at 60°C, gave good yields of alternating copolymer. Maximum rates of copolymerization were observed for a 1 : 1 monomer mixture.

Allyl-substituted aromatics, such as allylbenzene,<sup>(36–39)</sup> 2-allylphenol,<sup>(46)</sup> allyl-substituted fluorene,<sup>(40)</sup> and allylnaphthalene,<sup>(42)</sup> are also known to undergo equimolar copolymerization with MA. Both bulk<sup>(37,38)</sup> and solution<sup>(39)</sup> copolymerizations were studied. Copolymerization of an equimolar mixture of allylbenzene and MA at 59°C for 3 h, with 0.1 mol % AIBN, gave a low yield of alternating copolymer with an estimated molecular weight <5 000.<sup>(37)</sup> Using 2 wt. % *tert*-butyl peroxide initiator, a 1 : 1 monomer mixture, and running copolymerizations at 80, 100, 120, 140, and 160°C gave yields, respectively, of approximately 75, 35, 95, 88, and 82%. At the optimum temperature of 120°C, using initiator concentrations of 0.1, 0.5, 1.0, and 2%, it was found that the time necessary for full conversion of the monomers decreased with an increasing amount of initiator to 5 h at 2%. The white, amorphous allylbenzene–MA copolymer, prepared under optimum conditions, is soluble in ketones, insoluble in aromatics, has a softening temperature



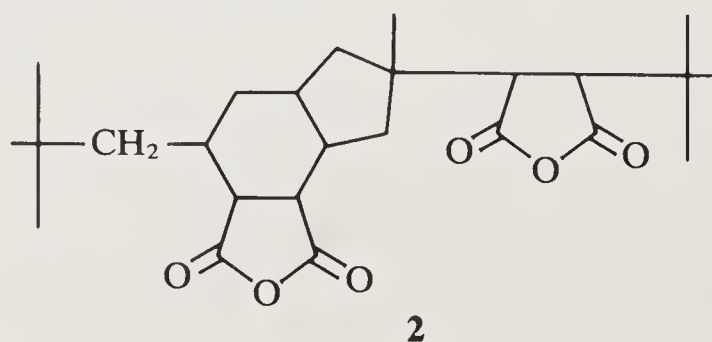
of 149–160°C, and an intrinsic viscosity, measured in dimethylformamide at 30°C, of 0.12 dl/g. In contrast, thermal polymerization (120°C) of a 1:1 allylbenzene–MA mixture for 15 h gave a 31% yield of copolymer, having a softening temperature of 123–139°C.<sup>(37)</sup>

Copolymerization of allylbenzene–MA mixtures in *N,N*-dimethylformamide (DMF) at 60°C also gives materials of constant composition, regardless of starting monomer ratios.<sup>(39)</sup> The copolymerization velocity is greatest for a MA concentration of 50 mol %. Allylbenzene, with  $Q = 0.019$  and  $e = -0.32$ , does not normally copolymerize with monomers having a negative  $e$  value.<sup>(39)</sup> However, copolymerization would be expected between allylbenzene and MA, since MA has  $Q = 0.230$  and  $e = 2.25$ .<sup>(41)</sup> An Arrhenius plot of polymerization velocities at various temperatures, using a fixed concentration of radical initiator and a 1:1 monomer mixture, showed a straight line for  $1/T$  and an activation energy of 24.2 kcal/mole.<sup>(39)</sup>

The copolymerization of 2-allylphenol (2AP) with MA, maleimide, and *N*-phenyl maleimide has been studied, both neat and in a variety of solvents, with several types of free-radical initiators.<sup>(46)</sup> Only the MA-2AP copolymers were equimolar for all starting feed ratios. The copolymerizations went best in halogenated and ketone solvents, with yields drastically reduced in *N,N*-dimethylformamide. The rates of copolymerization and yields were maximum at equimolar feed ratios. Also, addition of  $\text{ZnCl}_2$  or naphthalene to the reaction mixture gave increased yields. Copolymerization of an equimolar mixture of 2AP and MA in 1,2-dichloroethane for 5 h at 80°C, with 1% AIBN, gave an 87% yield of 1:1 copolymer. Addition of 0.5 mol % naphthalene increased the yield to 95%. The various copolymers had number average molecular weights, estimated by gel permeation chromatography, of 4 100–6 100. The acetoxy derivative of 2AP also copolymerized in a 1:1 fashion with MA. However, yields were less than using 2AP in the copolymerization.

Alternating copolymers of  $\alpha$ -allylnaphthalene with MA have received only brief study.<sup>(42)</sup> Heating equimolar amounts of the two monomers at 160–180°C, in the presence of 2–4 wt. % *tert*-butyl peroxide, gives a 77% yield of the 1:1 copolymer.

Allyl-substituted olefins, such as 3-allylcyclopentene forms a unique 2:1 copolymer with MA.<sup>(43)</sup> The copolymer, prepared in acetic anhydride solvent

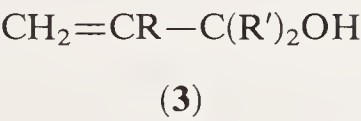




with AIBN initiator, is reported to have structure **2**. The rate of copolymerization was maximum for a 2 : 1 (MA : 3-allylcyclopentene) monomer feed ratio.

Silanes substituted with allyl groups are known to give alternating copolymers with MA.<sup>(44)</sup> Copolymerization of various mixtures of trimethylallylsilane and MA in benzene, with peroxide initiators, gave a material with 1 : 1 alternating monomer segments. In line with the discovery, the maximum copolymerization rate occurred at equimolar monomer feed and the reaction was first order with respect to the two monomers.

Allyl alcohol and derivatives of allyl alcohol readily undergo alternating cyclocopolymerization with MA to give materials soluble in polar solvents (Table 10.1). For the most part, these copolymers have a very high concentration of lactone ring structures and pendent carboxyl residues along the backbone of the polymer molecule (Table A.6).<sup>(32,33,45)</sup> The various monomers studied **3A–3E**, copolymerization conditions, yields, and other items are shown in Table 10.1.



- A

allyl alcohol (R = H, R' = H)
- B

methallyl alcohol (R = CH<sub>3</sub>, R' = H)
- C

2-phenylallyl alcohol (R = C<sub>6</sub>H<sub>5</sub>, R' = H)
- D

2-methylene propanediol (R = CH<sub>2</sub>OH, R' = H)
- E

1,1-dimethylallyl alcohol (R = H, R' = CH<sub>3</sub>)

Considering elemental analyses data, infrared absorption spectra with strong lactone absorption bands at 1 730–1 750 cm<sup>−1</sup> and carboxyl OH at 2 500–2 700 cm<sup>−1</sup>, solubility, and other factors for the various copolymers, structure **4** was assumed for the various materials.

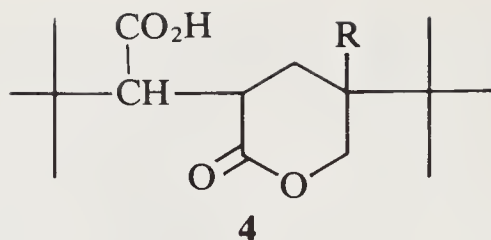
Table 10.1. Copolymerization of MA with Allyl Alcohol and Its Derivatives **3A–3E**<sup>a</sup>

Comonomer (3) <sup>b</sup>	Time (h)	Yield (%)	Melting point (°C)	[η] (dl/g)
A	48	82	230	0.080
B	5	100	300	0.026 <sup>c</sup>
C	5	100	310–330	0.221
D	48	62	240–300	—
E	48	5	135	—

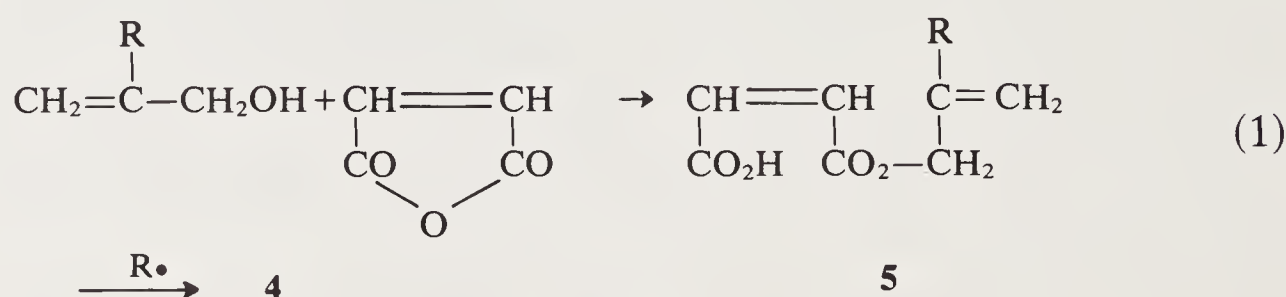
<sup>a</sup> After Reference 45. By permission of Hüthig and Wepf Verlag, Basel, Switzerland.

<sup>b</sup> Copolymerizations were run in dioxane at 70°C, using 1.0 wt. % AIBN.

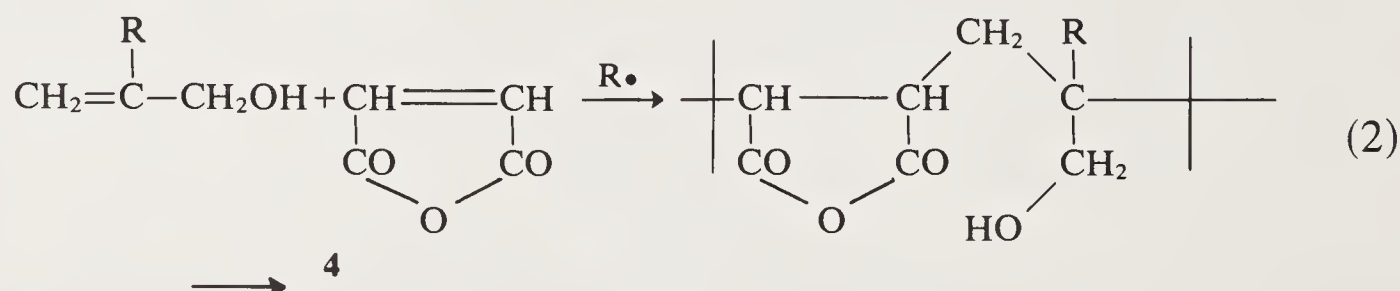
<sup>c</sup> Molecular weight = 18,000 (osmotic pressure method) or 43,000 (light-scattering method). Copolymers soluble in *N,N*-dimethylformamide, tetrahydrofuran, acetone, ethanol, pyridine, and dimethylsulfoxide.



Two copolymerization mechanisms may be visualized for polymer **4** formation: First, allyl alcohol is copolymerized with MA via the half-ester **5** as shown by Eq. (1).

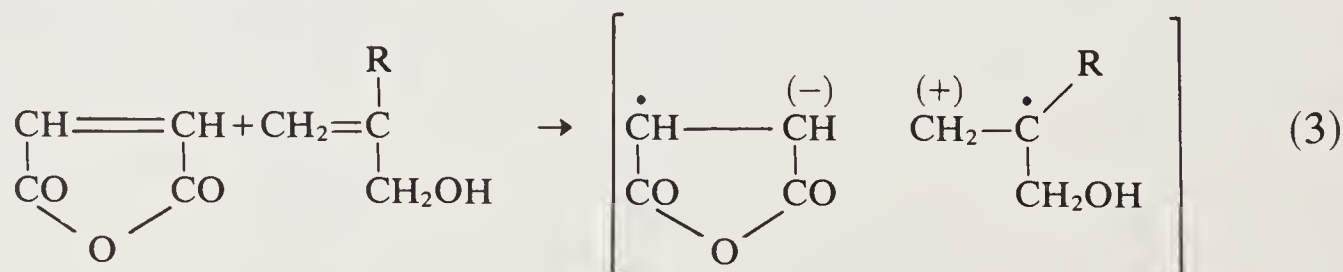


Second, allyl alcohol, is first copolymerized with MA and then esterification occurs to produce lactone rings, as shown by Eq. (2).

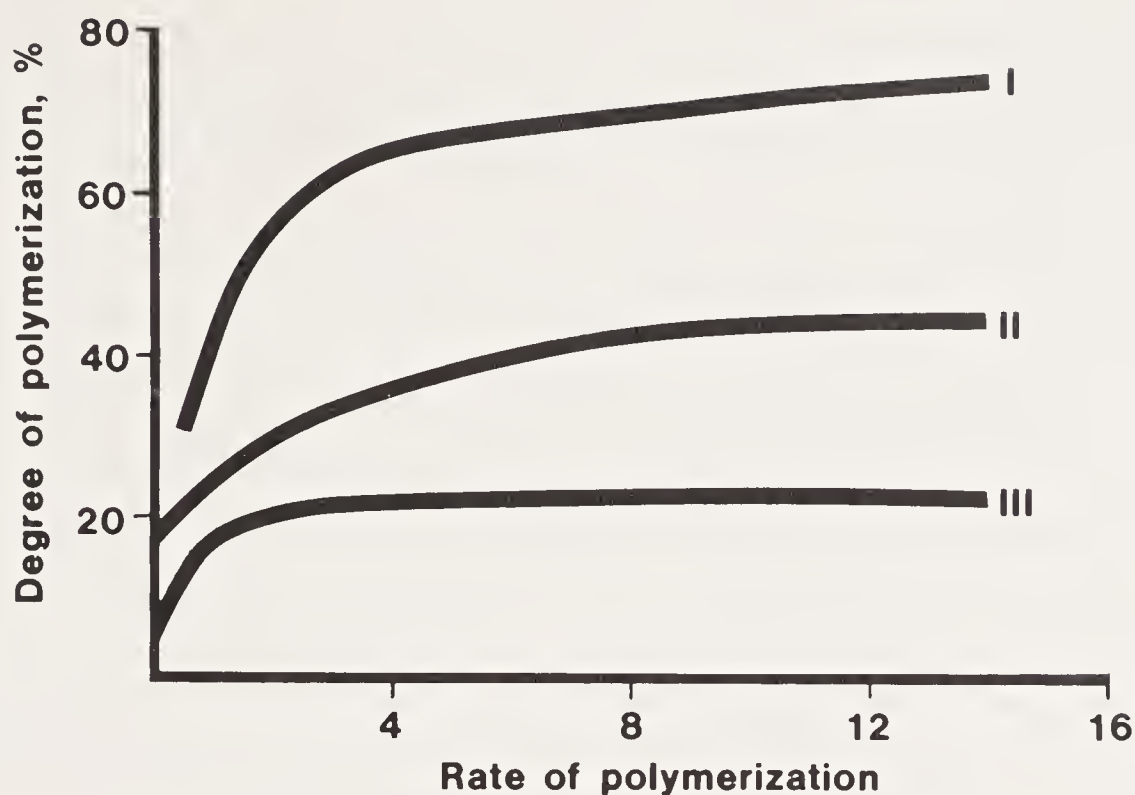


Based on the copolymerization information in Fig. 10-1, it is believed that the mechanism of the copolymerization is best represented by Eq. (2).

The results were interpreted to mean that the alternating copolymers are formed under the influence of a CTC existing between the allyl alcohol and MA.<sup>(45)</sup> Further, if the reaction is truly an alternative copolymerization and the CTC theory applies, it is reasonable to believe that a detailed mechanism should include the CTC shown in Eq. (3).



Methallylamine is reported to undergo free-radical copolymerization with MA.<sup>(47)</sup> It is speculated that this copolymer, which exhibits strong fluorescence, would also tend to have an alternating structure. It has also been shown that *N*-allylacetamide and monomethyl maleate mixtures, in the presence of  $\gamma$

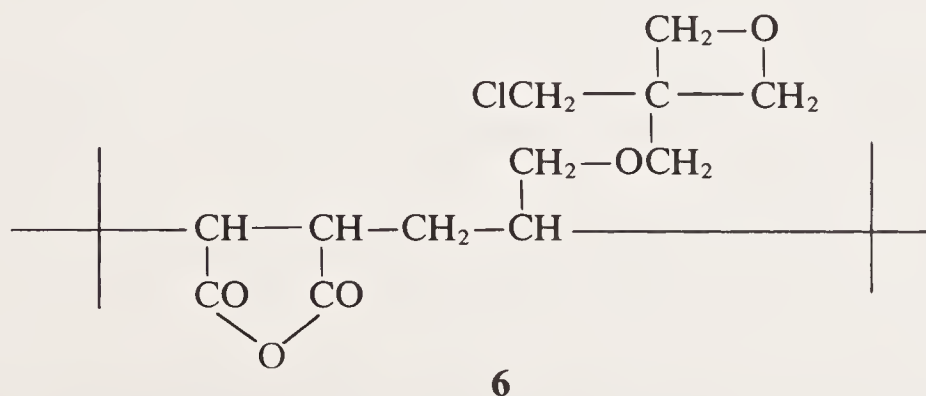


**Fig. 10-1.** Allyl alcohol-MA copolymerization. (I) MA and allyl alcohol were stirred at room temperature for about 48 h and thereafter AIBN was added at 70°C. Semiester not formed. (II) MA and allyl alcohol were stirred at 70°C for 48 h and thereafter AIBN was added at 70°C. Some semiester formed. (III) AIBN was added to semiester at 70°C. (After Reference 45. By permission of Hüthig and Wepf Verlag, Basel, Switzerland.)

radiation ( $^{60}\text{Co}$ ), have a strong tendency to give alternating copolymers.<sup>(448)</sup>

Several allyl ethers are known to undergo alternating copolymerization with MA.<sup>(48-51)</sup> The radical polymerization of MA with allyl glycidyl ether is claimed to occur by homopolymerization of the CTC formed from the monomer pair to give a copolymer having nearly equimolar composition.<sup>(48)</sup> Yields were good, when the BPO initiator was used and the copolymerization was run for 2 h at 60°C.

Free-radical-initiated copolymerization of 3-chloromethyl-3-allyloxy-methyl-oxetane with MA is believed to produce alternating copolymer **6**.<sup>(49)</sup>



In the absence of solvent, mixtures of the two monomers polymerize explosively in the presence of peroxides to give insoluble polymer. In contrast, copolymerization of the monomer pair runs smoothly in dioxane at 65°C, giving in 12.5 h an 83% yield of copolymer **6**, with a specific viscosity measured



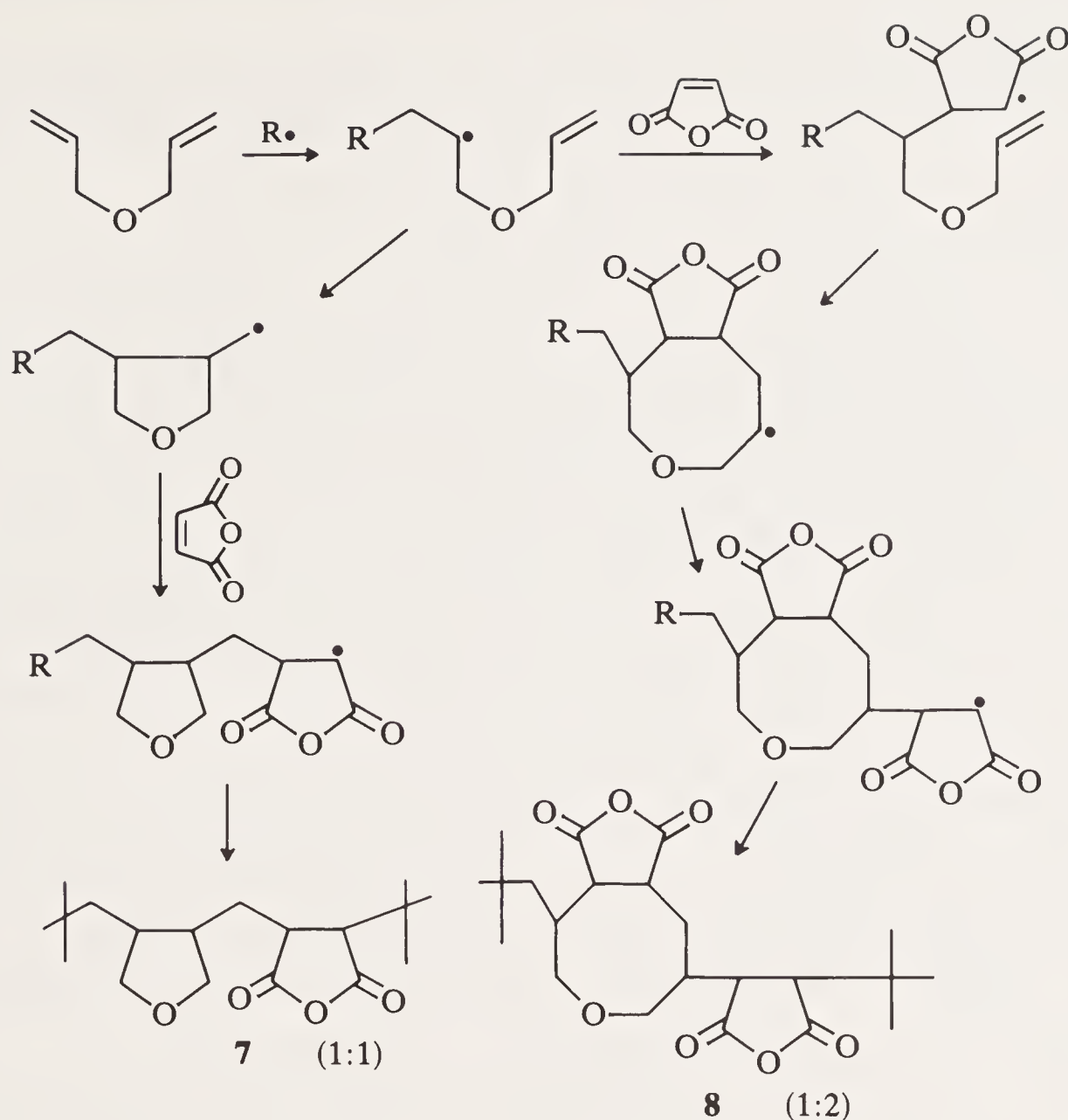
in acetone (0.4 g/100 ml, 30°C) of 0.068 dl/g. Since the allyl ether has  $Q = 0.030$  and  $e = -1.40$  and MA has  $Q = 0.23$  and  $e = 2.25$ , the two monomers would be expected to have a great desire to undergo alternating copolymerization.<sup>(49)</sup>

Halogenated allyl ethers, such as heptafluoroisopropyl allyl ether and heptafluoroisopropyl methallyl ether, also easily copolymerize with MA to give high-molecular-weight 1:1 copolymers.<sup>(50)</sup> In one example, equimolar amounts of the methallyl ether and MA were copolymerized with 0.01 mol % lauroyl peroxide to obtain a 75% yield of copolymer. The material had an inherent viscosity, measured in acetone at 25°C, of 0.75 dl/g and a weight average molecular weight, determined by light scattering, of 515 000.

Allylacetone, methallylacetone, 2-allylcyclohexanone, 1-phenyl-4-penten-1-one and other allyl substituted ketones, in the presence of free-radical initiators, copolymerize with MA to give equimolar copolymers in good yields.<sup>(46)</sup> Copolymerization with maleimides also occur but non-equimolar copolymers are obtained. The anhydride copolymers exhibit good solubility in many solvents, are compatible with many resin systems, and are useful for curing epoxy resins for castings and adhesives.

The monomers *N*-allylimidazole<sup>(47)</sup> and 2-allylpyrrole<sup>(52,53)</sup> are known to copolymerize with MA. The monomer 2-allylpyrrole, with  $Q = 0.07$  and  $e = -0.48$ , also copolymerizes with diethyl fumarate.<sup>(52,53)</sup> The structures of the copolymers have not been clarified. Analogous to the methallylamine copolymer, the *N*-allylimidazole copolymer also exhibits strong fluorescence.<sup>(47)</sup>

Akin to the well-known case for divinyl ether-MA copolymerization (Sec. 10.2.4, structures **19** and **20**), diallyl ether (DAE) also undergoes cyclopolymerization with MA and fumaronitrile.<sup>(51,478)</sup> The copolymerizations were run at 60°C in benzene and acetone solvent, using AIBN initiator. Under these conditions DAE fails to homopolymerize. The time-conversion curves showed that MA copolymerized much faster than fumaronitrile with DAE, with benzene solvent giving highest rates of polymerization. The IR and NMR spectra of the copolymers gave little or no evidence of the C=C double bonds in the copolymer. Based on copolymer composition, solubility, and IR and NMR spectra studies, cyclopolymerization of this monomer pair produces materials having cyclized 1:1 and 1:2 units, due to the proximity of the pendant double bond to the growing radical. Cyclization of DAE was not an exclusive reaction and the reaction to form cyclic 1:2 units only dominated when the concentration of MA was large. The observed limiting conversion with respect to the feed composition agreed with the theoretical limit of 1:1 copolymer when there was more DAE in the feed, and a theoretical limit of 1:2 copolymer when the feed was richer in anhydride. The suggested steps for the intermolecular-intramolecular alternating copolymerization, to form cyclocopolymer with units **7** and **8**, is shown.



### 10.2.2. Vinyl Ether Monomers

Both alkyl and aryl vinyl ethers and a variety of unsaturated cyclic ethers will undergo free-radical copolymerization with MA, under mild conditions, to give equimolar copolymers. DuPlessis and coworkers<sup>(176)</sup> have shown that dialkyl maleates and alkyl vinyl ethers will also undergo equimolar copolymerization. This occurs even though all of the monomers are very sluggish to free-radical homopolymerization. In some cases, spontaneous or thermal copolymerization can even occur between vinyl ethers and MA, such as 1,2-dimethoxyethylene,<sup>(54,55,450)</sup> *p*-dioxene,<sup>(55)</sup> and conjugated dihydro-anisole.<sup>(56)</sup> It is also known that vinyl ethers will polymerize in the presence of amide-MA mixtures, with the amide-MA CTC playing the role of initiator.<sup>(67,481)</sup>

Spontaneous copolymerization of vinyl ethers with MA are accelerated in the presence of trialkylaluminum compounds.<sup>(57)</sup> For example, spontaneous copolymerization of *n*-butyl vinyl ether-MA readily occurs in the presence of trioctylaluminum. Electron spin resonance, infrared, cryoscopic, and other analytical studies show that activation is achieved by the trioctylaluminum-







drofuran (THF) solvent, Endo *et al.*<sup>(73)</sup> determined the following viscosity–molecular weight equation for this copolymer.

$$[\eta] = 7.56 \times 10^{-4} \bar{M}_w^{0.55} \quad (\text{THF, } 30^\circ\text{C})$$

Copolymerization of MA with optically active alkyl vinyl ethers have received some attention, as a method to prepare optically active copolymers.<sup>(80–84)</sup> The study also helps to show the importance of steric effects in determining the configuration of a newly formed repeating unit in a polymer backbone. In one example, mixtures of *l*-menthyl vinyl ether, MA, and AIBN were combined in benzene solvent and irradiated (UV) at 30°C to obtain good yields of optically active copolymer. The best yield, 82%, and maximum rate of copolymerization were observed at approximately an equimolar monomer mixture.<sup>(81)</sup> Copolymerization in benzene at 50°C with free-radical initiation also produced a good yield of optically active copolymer.<sup>(85)</sup> The copolymers, with intrinsic viscosities in benzene at 30°C of 0.395–1.05 dl/g and polymer melt temperature of 208–212°C, had optical rotation  $[\alpha]_D$  values of –82 to –84.4. The alternating copolymers continued to be levorotatory even after cleavage of the *l*-menthyl residue,  $[\alpha]_D = -11.0$ , showing introduction of asymmetric carbon on the main chain. Copolymerization with maleates and fumarates also produced optically active equimolar materials.

Table 10.2. Alternating Copolymers of MA with Optically Active Alkyl Vinyl Ethers<sup>a,b</sup>

Code	$\begin{array}{c} \text{*CH} \text{---} \text{*CH} \text{---} \text{CH} \text{---} \text{CH}_2 \text{---} n \\   \qquad \qquad   \qquad   \\ \text{C} \qquad \qquad \text{C} \qquad \text{OR} \\ // \quad \backslash \quad / \quad // \\ \text{O} \qquad \text{O} \qquad \text{O} \end{array}$						
R	$\begin{array}{c}   \\ \text{CH}^* \text{---} \text{CH}_3 \\   \\ \text{CH}_2 \\   \\ \text{CH}_3 \end{array}$	$\begin{array}{c}   \\ \text{CH}^* \text{---} \text{CH}_3 \\   \\ \text{CH}_2 \\   \\ \text{CH}_2 \\   \\ \text{CH}_3 \end{array}$	$\begin{array}{c}   \\ \text{CH}_2 \\   \\ \text{*CH} \text{---} \text{CH}_3 \\   \\ \text{CH}_2 \\   \\ \text{CH}_3 \end{array}$	$\begin{array}{c}   \\ \text{CH}_2 \\   \\ \text{CH}_2 \\   \\ \text{*CH} \text{---} \text{CH}_3 \\   \\ \text{CH}_2 \\   \\ \text{CH}_3 \end{array}$	$\begin{array}{c}   \\ \text{CH}_2 \\   \\ \text{CH}_2 \\   \\ \text{CH}_2 \\   \\ \text{*CH} \text{---} \text{CH}_3 \\   \\ \text{CH}_2 \\   \\ \text{CH}_3 \end{array}$	$\begin{array}{c}   \\ \text{*CH} \text{---} \text{CH}_3 \\   \\ (\text{CH}_2)_5 \\   \\ \text{CH}_3 \end{array}$	$\begin{array}{c}   \\ \text{CH}_2 \\   \\ \text{CH}_2 \\   \\ \text{*CH} \text{---} \text{CH}_3 \\   \\ (\text{CH}_2)_3 \\   \\ \text{CH} \text{---} \text{CH}_3 \\   \\ \text{CH}_3 \end{array}$
Yield (%)	95	95	93	87	54	85	70
$[\eta]^c$ (100 ml/g)	0.66	0.60	0.30	0.89	0.88	0.79	1.00
$[\alpha]_D^{25\ d}$	+47.8	–44.0	+1.6	+17.9	+12.7	+54.4	–1.8

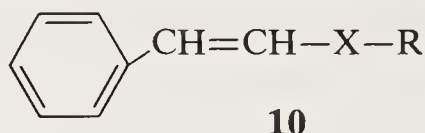
<sup>a</sup> After Reference 83. By permission of Pergamon Press Ltd., Headington Hill Hall, Oxford, England.  
<sup>b</sup> Copolymerizations run at 60°C with AIBN.  
<sup>c</sup> Determined in DMF at 30°C.  
<sup>d</sup> Molar optical rotation, determined neat.

Maleic anhydride has been copolymerized in benzene solution with seven different optically active alkyl vinyl ethers, having an asymmetric carbon atom at the  $\alpha$ ,  $\beta$ ,  $\gamma$ , or  $\delta$  position of the alkyl residue (Table 10.2).<sup>(82,83)</sup> Chemical compositions, solubilities of the polymer products, optical properties, and spectroscopic (IR and NMR) measurements confirmed the formation of copolymers with predominately alternating structure. The same authors<sup>(83)</sup> also showed that optically active 4-methyl-1-hexene could also be used to prepare optically active equimolar copolymer.

Copolymerization of isobutyl vinyl ether with MA in *l*-menthol, at 60°C with AIBN initiator, produces optically active, equimolar copolymer.<sup>(1126)</sup> This procedure, known as asymmetric induction polymerization, produced a copolymer with  $[\alpha]^{25}_D$  ranging from  $-0.13$  to  $-0.24$ .

Compared to alkyl vinyl ethers, the alternating copolymerization of aryl vinyl ethers with MA have had little study. In the simplest case, a 1:1 alternating copolymer of phenyl vinyl ether-MA is reported to be obtained in good yields by heating mixtures of the two monomers at 150°C.<sup>(86,625,1070,1129)</sup> Equimolar copolymerization should also occur at lower temperatures, both neat and in solution, by using free-radical initiators. The copolymer has been crosslinked with a small amount of divinylbenzene to prepare hydrophilic gels.<sup>(1088)</sup>

Styrene substituted in the  $\beta$  position with various alkyl ether or thioether residues **10**, i.e., 2-phenylvinyl alkyl ethers or thioethers, easily copolymerize with MA to give equimolar copolymers.<sup>(87-89,121,257,456,1067)</sup> The copolymers are being studied as rheology modifiers of petroleum.<sup>(121)</sup>



$\text{X} = \text{O}, \text{S}$

$\text{R} = \text{CH}_3, \text{CH}_2\text{CH}_3, \text{CH}_2\text{CH}_2\text{CH}_3, (\text{CH}_2)_3\text{CH}_3, \text{CH}(\text{CH}_3)_2, \text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_3,$   
 $\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_3, \text{CH}_2\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_3$

Bulk and solution copolymerizations at 70°C, using equimolar mixtures and AIBN initiator, produced alternating ether copolymers in 54–76% yields and number average molecular weights of 28,000–60,000. The rates of copolymerization were largely dependent on the bulkiness of the alkyl groups in the phenylvinyl alkyl ether series. Spontaneous copolymerization did not occur, but 2-phenylvinyl ethyl ether copolymerizes with MA in the presence of oxygen.

Molecular weights increased with conversion in the phenylvinyl alkyl ether-MA copolymerizations. Under comparable conditions, lower copolymer yields were obtained for the vinyl thioether-MA pairs. Yields and molecular weight, in both cases, were shown to be highest when equimolar amounts of



monomers were combined for polymerization. Peroxide initiators gave reduced yields and molecular weights for the vinyl ether copolymers and failed to bring about copolymerization for the vinyl thioethers. The phenylvinyl thioethers also failed to copolymerize with MA when oxygen was present. The ether-MA copolymers had polymer melt temperatures (pmt) of 228–290°C and intrinsic viscosities, measured in 2-butanone at 25°C, of 0.23–0.60 dl/g; whereas, the thioether copolymers, evaluated in the same manner, had a pmt range of 200–275°C and intrinsic viscosities of 0.04–0.06 dl/g.

For the 2-phenylvinyl ethyl ether-MA copolymer, having a polymer melt temperature of 275°C, an intrinsic viscosity of 0.49 dl/g was equivalent to a number average molecular weight ( $\bar{M}_n$ ) of 60,000. The corresponding sulfur-containing copolymer, prepared in the same manner, exhibited a pmt of 245°C, glass transition temperature ( $T_g$ ) of 218°C, and  $\bar{M}_n = 5\,000$ . Fles and coworkers<sup>(88,89,1067)</sup> believe that the polymerization results are in agreement with a combined free-monomer CTC mechanism, since none of the monomers homopolymerized under the conditions used; the mixtures readily copolymerized and alternating copolymers were formed under extreme conditions of comonomer unequivalency.

*Cis*- and *trans*-isomers of methyl propenyl ether, structurally similar to 2-phenylvinyl methyl ether, also undergo equimolar copolymerization with MA.<sup>(90)</sup> Under the conditions of the study, i.e., benzene solvent, free-radical initiator, and 60°C polymerization temperature, the *cis*-isomer was shown to be the most reactive. The orders of the two monomers toward the MA radical ( $1/r_1$ ) were *cis* = 0.431 and *trans* = 0.347. The specific viscosities of the copolymers, measured in acetone at 30°C, varied from 0.11 to 0.42 dl/g. Alternating copolymers were obtained over a wide variation of monomer feed ratios.

Internal olefins with alkyl ether substituents at both 1 and 2 positions, such as *cis*- and *trans*-1,2-dimethoxyethylene, because of greatly increased electron-donor capability undergo spontaneous alternative copolymerization with MA, even at 10°C.<sup>(54,55,91,92)</sup> In fact, the yellow-colored monomer mixtures gradually polymerize when left standing in air a short time at room temperature to form a dense viscous liquid.<sup>(91)</sup> In every case, the dimethoxyethylene-MA copolymer compositions were essentially constant, regardless of the monomer compositions and maximum copolymerization rates were observed close to the 1:1 monomer feeds. Comparison of the copolymerization reactivities indicated that the rates were similar for the two isomers but at around 1:1 monomer compositions the polymerization rate was highest for the *cis*-isomer. The monomer 2,2-dimethyl-1,3-dioxole, structurally similar to dimethoxyethylene, also undergoes facile free-radical copolymerization with MA to give equimolar copolymer.<sup>(97)</sup>

To examine copolymerization rates, equimolar amounts of dimethoxyethylene and MA were combined and polymerized in benzene at



40, 50, and 60°C, using 0.1 mol % AIBN. The copolymerization conversion rate was 0.20%/min at 40°C, 1.09%/min at 50°C, and 4.71%/min at 60°C. These results were fitted to a straight line using the Arrhenius equation, with the data showing an activation energy for copolymerization of 32.8 kcal/mol.<sup>(55)</sup> This is about 10 kcal/mol higher than the activation energy of typical copolymerization reactions. At 80°C, copolymerization was complete almost instantaneously, even in the presence of only 0.01 mol % initiator. The dimethoxyethylene-MA copolymers are white powders, soluble in polar solvents, having softening points in the range 210–250°C and start to decompose at approximately 240°C.

The monomer  $\beta$ -*N*-carbazolyethyl vinyl ether is known to copolymerize with MA or *N*-substituted maleimides in the presence of free-radical initiators.<sup>(93)</sup> Copolymerizations were run in benzene for 24 h at 60°C, producing low-molecular-weight MA copolymer in an 80% yield and maleimide copolymer in 27–84% yields. Color, due to CTC formation, was observed on mixing the monomer solutions; however, spontaneous copolymerization was not observed. Charge-transport properties of the copolymers were measured and discussed, using xerographic discharge techniques.

### 10.2.3. Cyclic Ether Monomers

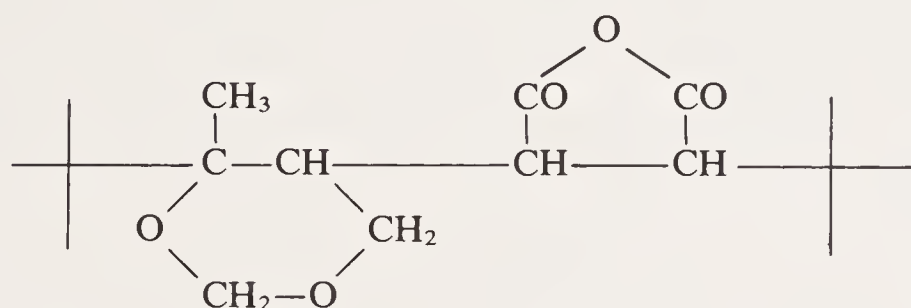
Several different types of unsaturated cyclic ethers, such as *p*-dioxene, 2,3-dihydropyran, furan, 2-methylfuran, 2,3-dihydrofuran, 2,2-dimethyl-1,3-dioxole, 2-methylene-oxetane, and benzofuran have been copolymerized with MA. Only the 2-methylene-oxetane fails to copolymerize in a 1:1 fashion with MA.

The alternating copolymerization of *p*-dioxene with MA has received substantial study.<sup>(54,55,91,94–96,98,99,450)</sup> Similar to other vinyl ethers, *p*-dioxene is not amenable to free-radical-initiated homopolymerization. However, polymerization of the yellow-colored solution of the two monomers occurs readily with or without a free-radical initiator. Copolymerization is inhibited by standard free-radical inhibitors, such as hydroquinone. Copolymerizations of monomer mixtures have been examined both neat and in a variety of solvents, using AIBN at 60°C.<sup>(96)</sup> As expected, the rate of copolymerization and the reduced viscosity of the copolymer depends on the monomer feed ratio and have their maximum at a 1:1 monomer mixture. In addition, alternating copolymers were obtained regardless of the monomer mixture ratio.

Studies show that the *p*-dioxene-MA copolymerization rate is considerably lower than that of 1,2-dimethoxyethylene-MA, i.e., less than  $\frac{1}{6}$ . A comparison of the various copolymerization rates showed *cis*-1,2-dimethoxyethylene > *trans*-1,2-dimethoxyethylene > *p*-dioxene.<sup>(91)</sup> Steric effects are advanced to account for the apparent sixfold lower reactivity of

*p*-dioxene as compared with 1,2-dimethoxyethylene. The apparent activation energy for the free-radical-initiated *p*-dioxene copolymerization was estimated to be 22 kcal/mol,<sup>(91)</sup> about equal to values reported for typical vinyl polymerizations and comparing well with activation energies of 23.0 and 21.5 kcal/mole previously reported, respectively, for the dodecyl vinyl ether-MA<sup>(100)</sup> and *n*-butyl vinyl ether-MA<sup>(504)</sup> systems. An overall activation energy of 14.5 kcal/mole has also been reported for spontaneous copolymerization of *p*-dioxene with MA.<sup>(54)</sup>

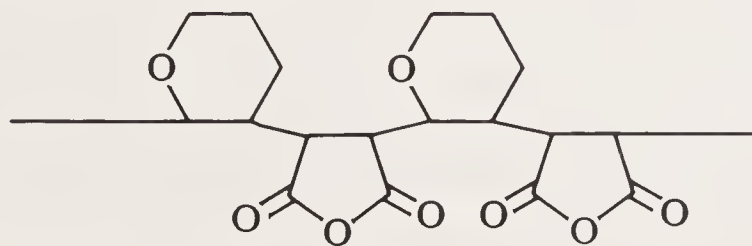
The monomers 4-methyl-1,3-dioxene-4<sup>(101)</sup> and 2-trichloromethyl-4-methylene-1,3-dioxolane<sup>(1128)</sup> and other 4-methylene-1,3-dioxolanes<sup>(1132)</sup> are known to also undergo spontaneous copolymerization, with MA at temperatures >50°C, giving good yields of low-molecular-weight, alternating copolymer. The equimolar 4-methyl-1,3-dioxene-4-MA copolymer structure **11** is shown below.



**11**

Using molecular orbital concepts,<sup>(102)</sup> the  $\pi$ -extension model, and the various transition states in the copolymerization process, it was clearly established that the cross-propagation reactions were very much preferred over the homopropagation reactions.<sup>(101)</sup> The  $\pi$ -extension model was shown to be sufficient to account for the alternating copolymerization of the monomer pair to give **11**.<sup>(101)</sup> It would be of value to find out if the  $\pi$ -extension model could also be used to account for other alternating copolymerizations of MA with electron-donor monomers.

Several groups have studied the copolymerization of dihydropyran with MA.<sup>(65,66,90,103)</sup> When equimolar mixtures of the two monomers are combined and heated on a steam bath, either neat or in benzene solvent, a 1 : 1 copolymer **12** is obtained in approximately 85% yield.<sup>(103)</sup> Using an equimolar mixture,



**12**

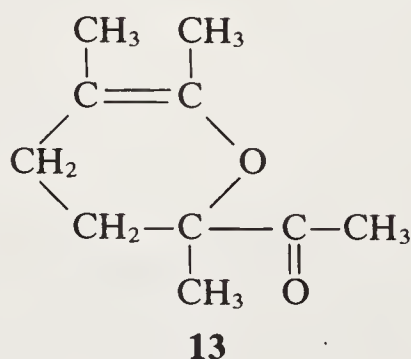
chloroform solvent, BPO initiator, and running the polymerization at 60°C gave alternating copolymer with relative viscosity ( $\eta_{rel}$ ) in acetone



(0.5 g/100 ml, 30°C) of 1.025 dl/g. Similar to the *p*-dioxene system, the rate of copolymerization of the dihydropyran-MA pair is also significantly less than the rates of copolymerization of *cis*- and *trans*-1,2-dimethoxyethylenes or *cis*- and *trans*-methyl propenyl ethers with MA.<sup>(90)</sup>

Two substituted dihydropyrans are also reported to undergo equimolar copolymerization with MA. In the first example, 2-glycidoxy-2,2-dihydropyran copolymerizes with MA to give high yields of insoluble copolymer.<sup>(104)</sup> The crosslinked product indicates that both copolymerization and copolycondensation reactions occur under the conditions studied.

In the second example, methyl isopropenyl ketone exists as a cyclodimer **13**, and although this monomer will not undergo free-radical-initiated homopolymerization, it will readily copolymerize with MA.<sup>(105)</sup> Mixtures of the cyclodimer **13** and MA form a yellow-colored solution in benzene and exhibit a strong absorbance maximum in the ultraviolet at 360 nm. The copolymers, prepared neat at 60–80°C with AIBN, are not strictly 1:1 alternating. The apparent activation energy was determined as 2.2 kcal/mol.<sup>(105)</sup> Methyl vinyl ketone dimer is also reported to undergo equimolar copolymerization with MA.<sup>(512)</sup>



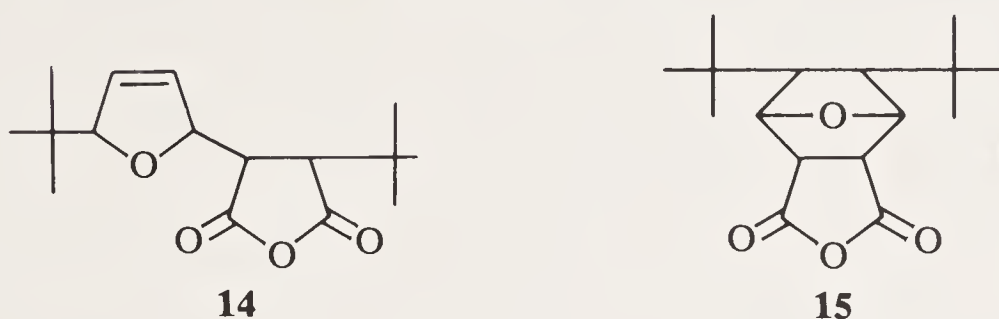
(2-Acetyl-2,5,6-trimethyl-2,3-dihydropyran)

Several groups have studied the copolymerization of furan,<sup>(106–112,503,1125)</sup> 2-methylfuran,<sup>(107,1125)</sup> and 2,5-dimethylfuran<sup>(1125)</sup> with MA. Copolymerizations may be achieved under both free-radical and radiation (<sup>60</sup>Co  $\gamma$ -source) conditions but fails under ultraviolet radiation even with photosensitizers.<sup>(107)</sup> The equimolar copolymer can also be formed by heating the furan-MA Diels-Alder adduct (see Chapter 4) in the presence of free-radical initiators at temperatures >60°C, suggesting a retrograde reaction gives the two monomers which subsequently copolymerize via some type of CTC formation.<sup>(107)</sup> In benzene solvent at 70°C and using AIBN initiator, poly(furan-co-MA) has been produced with intrinsic viscosities in 2-butanone (0.5 g/100 ml, 25°C) as high as 0.12 dl/g and pmt range of 185–210°C.<sup>(108)</sup> Under the same conditions, 2-methylfuran gave copolymer with  $[\eta] \leq 0.33$  dl/g and pmt 265–275°C.<sup>(107)</sup>

At one time some disagreement existed over the possible copolymerization mechanism and structure for the alternating furan-MA copolymer. Two structures, **14** and **15**, were suggested.<sup>(106,108,112)</sup> To find answers for the

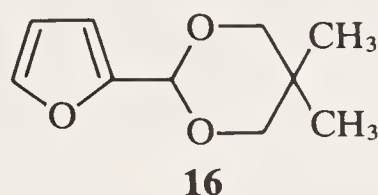


discrepancies that existed between the results and conclusions of Gaylord and coworkers<sup>(107,108)</sup> and those of Kamo and coworkers<sup>(112)</sup> the free-radical-initiated copolymerization of the furan-MA pair, as well as the homopolymerization of the furan-MA Diels-Alder adduct, were reinvestigated.<sup>(503)</sup> It is now known that both structures **14** and **15** can be obtained, depending on



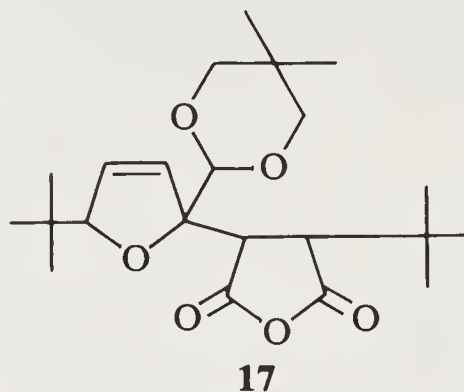
starting materials used and polymerization conditions.<sup>(503)</sup> Copolymerization of the pair in the presence of a perester or AIBN at 50 or 70°C yields copolymer **14**. When the Diels-Alder adduct is heated in solution at 70°C with free-radical initiators, copolymer **14** is also obtained, due to retrograde dissociation of the adduct. The structure of copolymer **14** was confirmed by bromination and <sup>1</sup>H and <sup>13</sup>C NMR studies.<sup>(110,111,503,1125)</sup> Clarification of the discrepancy occurred when Gaylord and coworkers<sup>(503)</sup> showed that the Diels-Alder adduct would homopolymerize in the presence of a rapidly decomposing perester at 50°C, giving copolymer **15**. Under these conditions retrograde dissociation of the adduct did not occur. Vazzana and coworkers<sup>(109)</sup> also reported that copolymer **14** could be produced by exposure of furan-MA mixtures to  $\gamma$  radiation (<sup>60</sup>CO) at 20°C. In contrast, the adduct did not polymerize under  $\alpha$  irradiation at 20°C due to lack of retrograde dissociation of the adduct. The structure of copolymer **15** was also confirmed by elemental, IR, NMR, etc., studies.<sup>(503)</sup>

The monomer 2-furyl-5,5-dimethyl-1,3-dioxane **16** and MA copolymerize in dioxane or benzene solution with AIBN to yield soluble copolymers.<sup>(114)</sup>



No copolymer was generated when the initiator concentration was below 0.06 mole/liter or the reaction temperature below 55°C. Holding the total monomer feed constant and varying the monomer feed ratio systematically, a series of low conversion copolymers were prepared. The copolymer compositions, as shown by elemental analysis, was independent of monomer feed composition and the molar ratio of the two monomers in the copolymer was essentially unity. The number average molecular weights for the series varied from 2 250 to 3 165, with the 3 165 value found for the equimolar feed case.

The softening range of the copolymers varied over the range 280–320°C. The structure of the copolymer **17** was identified by chemical analysis, NMR, and IR spectroscopy.<sup>(114)</sup>

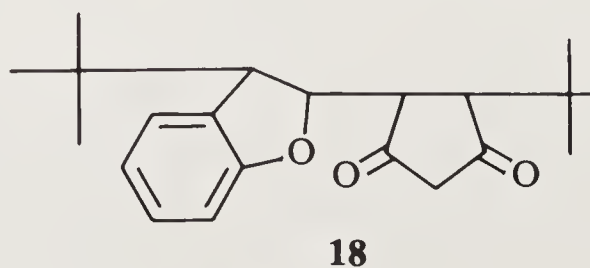


Mixtures of 2,3-dihydrofuran and MA turn yellow and spontaneously polymerize to yield a 1:1 alternating copolymer.<sup>(115)</sup> The reaction is highly exothermic. As copolymerization progresses the yellow color of the CTC slowly fades. The polymerization proceeds homogeneously in acetone solvent and heterogeneously in benzene or chloroform (polymer precipitates). In solution polymerization the color also fades during polymerization, becoming almost colorless when the yield of copolymer reached a maximum. Bulk copolymerization gave the best yields. The copolymer produced in acetone had a reduced viscosity of 0.61 dl/g (0.2 g/100 ml DMF, 25°C). When run in acetone at 60°C, the spontaneous polymerization rate ( $R_p$ ) equation has the following character:

$$R_p = 2.4[2,3\text{-Dihydrofuran}]^{1.99}$$

The copolymerization conversion rate data were fitted to a straight line using the Arrhenius equation, and an activation energy of 16.3 kcal/mol was found.<sup>(115)</sup>

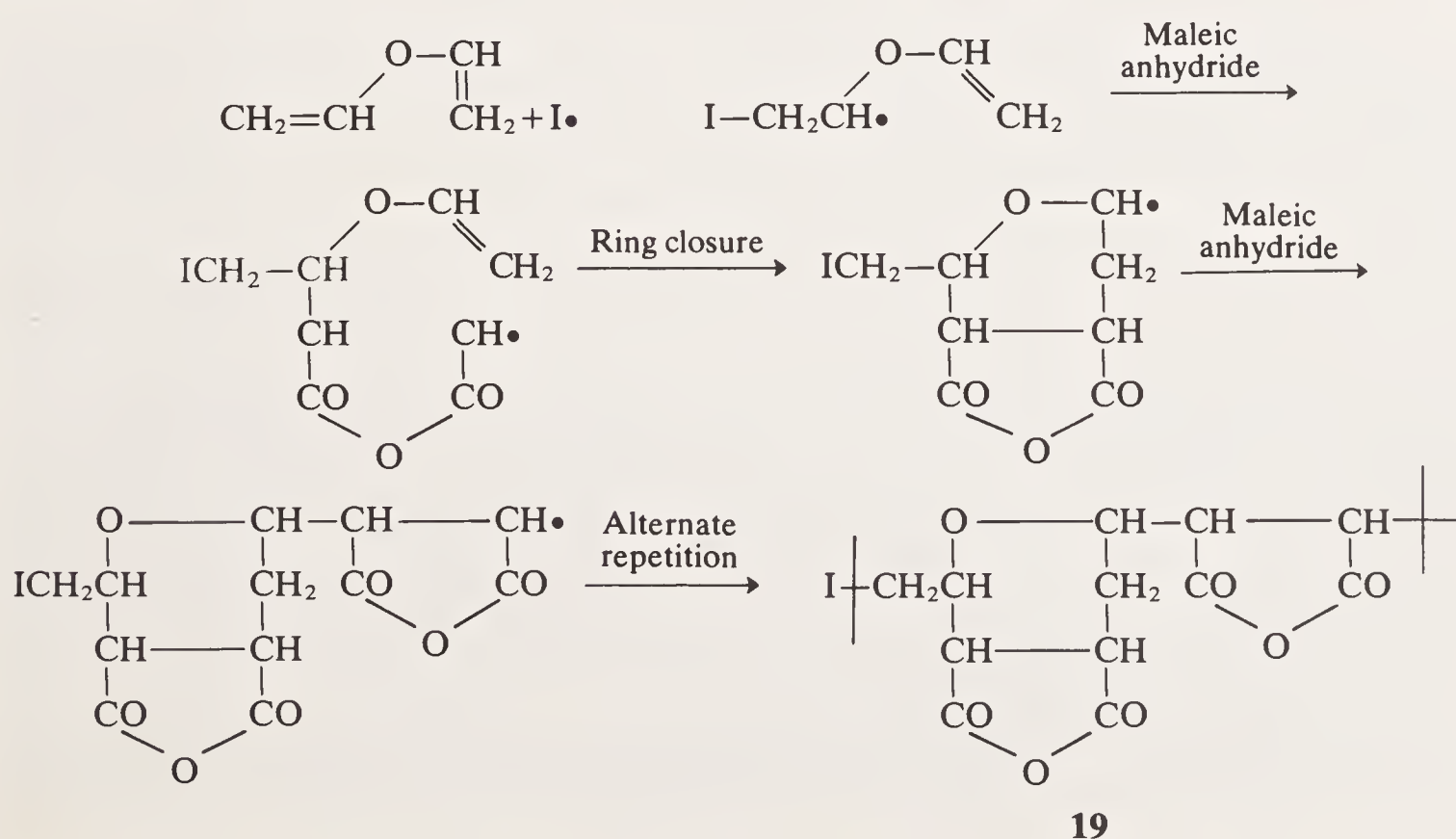
Benzofuran copolymerizes with MA, using AIBN initiator, to give a good yield of equimolar copolymer **18**.<sup>(116,117)</sup> Essentially a quantitative yield of low-molecular-weight polymer, with a reduced viscosity measured in acetone (0.5 g/100 ml at 25°C) of 0.11 dl/g, was obtained in 16 h at 60°C. The rate was greatest for a 1:1 monomer feed. The copolymer structure **18** was confirmed by NMR.



Isopropenyl-substituted furan and benzofuran have been bulk copolymerized with MA at 65–70°C, using peroxide initiators.<sup>(118)</sup> The copolymer structures were not investigated. However, the use of equimolar feeds causes one to assume that 1:1 copolymers were produced.

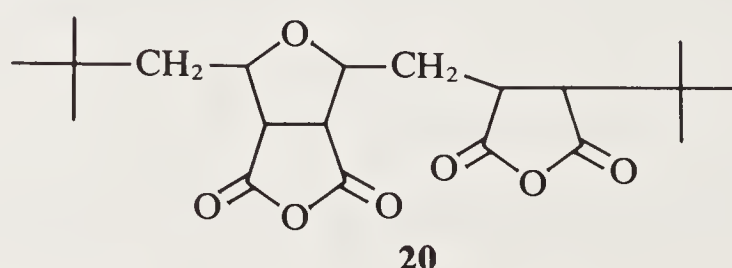


1,3-Dioxep-5-ene or 2-alkyl substituted 1,3-dioxep-5-enes copolymerize with MA, in the presence of free-radical initiators, to give 1 : 1 copolymer in good yields.<sup>(15,1131)</sup> Copolymerization fails with maleates and fumarates and gives nonequimolar copolymer with maleimides. Complete hydrolysis of the 1 : 1 copolymer, under acidic conditions, produces head-to-head poly(4-hydroxycrotonic acid). The poly(4-hydroxycrotonic acid) is hard to isolate, converting readily with heat to a head-to-head polylactone. When heated (>200°C), aldehyde is eliminated from the 1,3-dioxep-5-ene-MA copolymer giving soluble polymer with lactone rings. The 1,3-dioxep-5-ene-MA copolymer may also be heated in acidified isopropyl alcohol-water mixture to obtain a slurry of the head-to-head poly(crotonlactone).





Studies by Samuels<sup>(122)</sup> shed further light on the possible structure of the divinyl ether-MA copolymer. The methyl ester of the 1:2 copolymer was used as a molecular probe to identify the anhydride copolymer structure. By esterifying the 1:2 copolymer, it was possible to produce a situation wherein the solution behavior of the esterified product would be vastly different from the parent copolymer. Solution light-scattering, gel permeation chromatography, and intrinsic viscosity measurements show that tetrahydrofuran at 30°C is a theta solvent for the copolymer, and that the copolymer has a random coil conformation. Determination of the characteristic ratio of the copolymer required identification of its molecular structure. Molecular model studies showed that the bulky methyl ester groups cause much more steric hindrance in the generally accepted tetrahydropyran structure of the copolymer than an alternative tetrahydrofuran structure. These observations, together with the copolymer's solution properties, show the tetrahydrofuran structure could be more in accord with experimental data. Thus, Samuels<sup>(122)</sup> suggested that the 1:2 divinyl ether:MA copolymer most likely contains tetrahydrofuran rings in the structure **20**. Recent <sup>13</sup>C NMR studies by Tsukino and Kunitake,<sup>(1133)</sup> on cis-propenyl vinyl ether, 2-methylpropenyl vinyl ether, and cis-dipropenyl ether-MA copolymers support Samuels<sup>(122)</sup> conclusions. However, the latest work by Butler and Chu,<sup>(123)</sup> using proton NMR and <sup>13</sup>C-NMR, supports a chair-form, six-membered ring structure with predominantly *trans* geometry in the anhydride ring **19**.

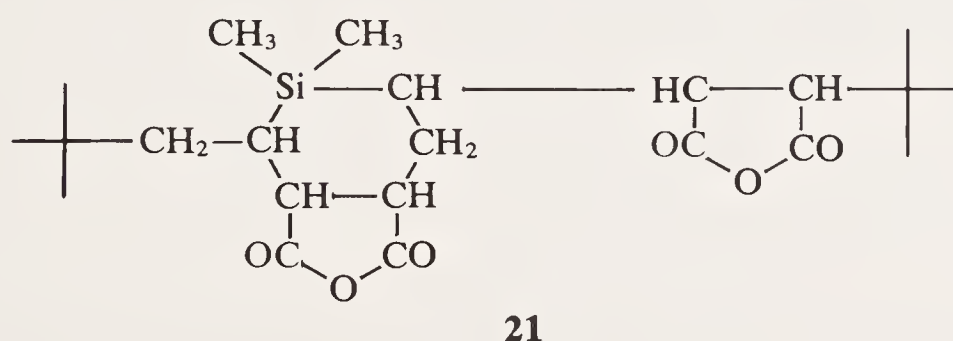


Initially only low-molecular-weight PYRAN type materials, having low intrinsic viscosities in *N,N*-dimethylformamide (DMF) and 2*N* sodium hydroxide, were obtained. These materials were also soluble in acetone and exhibited a melting point, with decomposition, at approximately 350°C. Procedures are now known for preparing high-molecular-weight materials.<sup>(124)</sup> For example, using dichlorobenzoyl peroxide initiator, benzene solvent, and a 1:2 molar mixture of divinyl ether:MA, copolymers may be obtained with inherent viscosities in DMF (0.4 g/100 ml, 25°C) as great as 1.69 dl/g. In all cases, the copolymers analyze for approximately a 1:2 molar mixture of divinyl ether:MA and exhibit solubility in concentrated sulfuric acid and DMF and dissolve with reaction in dilute aqueous alkali and alcohols. High-molecular-weight materials do not melt but soften at about 230°C and start to decompose at approximately 300°C.<sup>(124)</sup>

Dimethyl fumarate and diethyl maleate are also capable of undergoing alternating copolymerization with divinyl ether.<sup>(120)</sup> Also, chloromaleic anhy-

drude is reported to undergo free-radical-initiated copolymerization with divinyl ether to give saturated 1:1 copolymer.<sup>(525)</sup> Divinyl monomers with a nitrogen heteroatom, such as *N,N*-divinylaniline, are also reported to have a strong tendency to copolymerize in a 1:1 fashion with dialkyl fumarates.<sup>(1033)</sup>

The very interesting antitumor and interferon inducer properties of PYRAN copolymer (a product of Hercules, Inc.)<sup>(120,122)</sup> helped to foster interest in studying the copolymerization of other divinyl monomers with MA. Compounds such as divinyl sulfide,<sup>(1088)</sup> divinyl sulfone,<sup>(122,124,125)</sup> divinyl-dimethylsilane,<sup>(126)</sup> divinylcyclopentamethylenesilane,<sup>(125)</sup> hydroquinone divinyl ether,<sup>(127,1073)</sup> diethylene glycol divinyl ether,<sup>(127)</sup> 1,2-bis(ethenyl-oxy)benzene, and 1,2-bis(2-ethenyloxy ethoxy) benzene<sup>(1119)</sup> have received attention. In general, copolymers of these monomers with MA have not exhibited molecular weights as high as the first described PYRAN copolymers. Only crosslinked materials could be obtained from the copolymerization of diethylene glycol and hydroquinone divinyl ethers with MA. For the most part, elemental, NMR, IR, and other analytical data were consistent with the 1:2 divinyl monomer:MA monomer ratio in the copolymer. All analytical data support a 1:2 structure **21** as most representative of the dimethyldivinylsilane-MA copolymer. None of these materials have received the same attention or interest as PYRAN copolymers. However, they do further illustrate



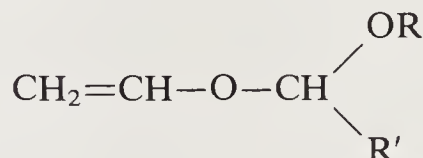
the great versatility that polymer chemists have for preparing alternating copolymers.

### 10.2.5. Vinyl Acetals

Both linear and cyclic acetals with vinyl residues copolymerize in an alternating fashion with MA. Two good examples are the copolymers prepared from the *O*-vinyl acetals of formaldehyde or acetaldehyde<sup>(128)</sup> and 2-vinyl-1,3-dioxalane.<sup>(129,130)</sup> The monomer 4-methylene-2-(trichloromethyl)-1,3-dioxolane also copolymerizes in a 1:1 fashion with MA, regardless of the initial monomer feed ratio in the reaction mixture, duration of reaction time, and monomer conversion.<sup>(1128)</sup> 1,3-Dioxep-5-enes are also cyclic acetals. The copolymerization of these monomers with MA<sup>(15,1131)</sup> was discussed in Sec. 10.2.3.



A variety of *o*-vinyl acetals of formaldehyde and acetaldehyde, **22A–22G**, have been prepared and copolymerized with MA.<sup>(128)</sup>



**22**

**A** R = C<sub>2</sub>H<sub>5</sub>, R' = H

**B** R = CH(CH<sub>3</sub>)<sub>2</sub>, R' = H

**C** R = C(CH<sub>3</sub>)<sub>3</sub>, R' = H

**D** R = C<sub>6</sub>H<sub>5</sub>, R' = H

**E** R = CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>, R' = H

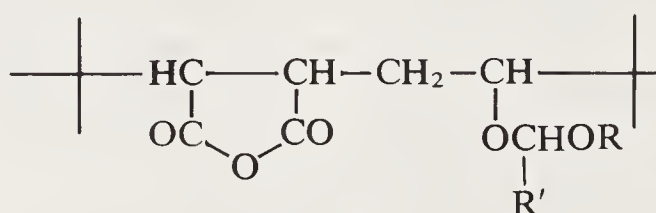
**F** R = C<sub>2</sub>H<sub>5</sub>, R' = CH<sub>3</sub>

**G** R = Iso-C<sub>4</sub>H<sub>9</sub>, R' = CH<sub>3</sub>

These monomers could easily be considered as additional examples of vinyl ether type monomers. Thinking in this vein, these monomers **22** would be expected to exhibit homo and copolymerization characteristics similar to the vinyl ethers—i.e., homopolymerize poorly with free-radical initiators and copolymerize readily with MA.

As expected, **22A–22G** monomers do homopolymerize poorly with free-radical initiators. For example, formaldehyde-*o*-vinyl-*o*-phenylacetal **22D**, which exhibits free-radical-initiated homopolymerizability, was converted with AIBN to only a 24% yield of polymer after 10 days in toluene at 55°C.

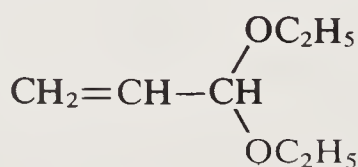
All seven monomers, **22A–22G**, copolymerized easily with MA to give good yields of equimolar copolymers **23**.



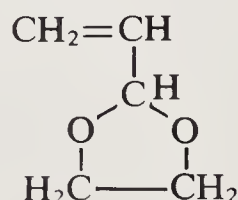
**23**

Considering only one example, an equimolar mixture of **22D** and MA converts to a 100% yield of copolymer when heated in toluene for 2–3 h at 55–60°C, with 1.0 wt. % AIBN initiator. In the preparation, the solid polymer precipitates rapidly from the toluene after only a few minutes reaction time.<sup>(128)</sup>

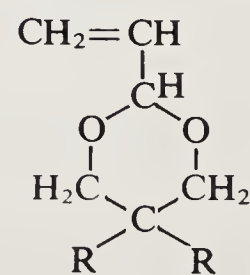
Linear and cyclic acetals with vinyl unsaturation are easily prepared from acrolein and alcohols or glycols. Monomers such as acrolein diethylacetal **24**,<sup>(131)</sup> 2-vinyl-1,3-dioxalane **25**,<sup>(129)</sup> and 2-vinyl-1,3-dioxane **26**<sup>(130,131)</sup> are allylic in nature and not very amenable to homopolymerization by free-radical initiators, due to the well-known phenomenon of “degradative chain transfer.”



**24**



**25**



**26**

R = H, CH<sub>2</sub>OH, CH<sub>3</sub>

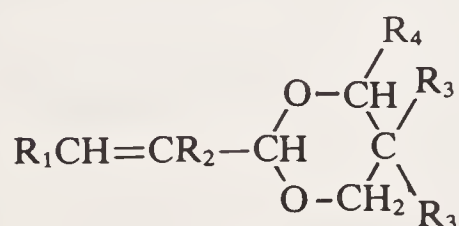


Acrolein diethylacetal **24** and MA were copolymerized in benzene with free-radical initiation to obtain a remarkably uniform composition (1:1), regardless of the monomer feed ratios.<sup>(131)</sup> It was suggested that the CTC brought about the alternating copolymerization.

The copolymerization of various mixtures of 2-vinyl-1,3-dioxalane **25** and MA were studied at 60°C, using BPO initiator.<sup>(129)</sup> The copolymer compositions, with conversions being held below 7%, varied slightly with the monomer feed compositions and with monomer concentration. From the fact that both the copolymerization rate and absorption in the ultraviolet spectra of the monomer mixtures were maximum at a 1:1 monomer mixture, Ouchi and Oiwa<sup>(129)</sup> concluded that copolymerization might well proceed via a CTC.

Copolymerizations of 2-vinyl-1,3-dioxane **26** (R = H), 5,5-bis(hydroxymethyl)-2-vinyl-1,3-dioxane **26** (R = CH<sub>2</sub>OH), and 5,5-dimethyl-2-vinyl-1,3-dioxane **26** (R = CH<sub>3</sub>) with MA were studied in benzene at 65°C, using BPO initiator.<sup>(130,132)</sup> In all three cases, copolymerization of the cyclic acetals with MA resulted in copolymers having essentially perfectly alternating sequences, independent of the starting monomer compositions. Also, the maximum rate of copolymerization was observed at 1:1 monomer feeds. The study suggests that degradative chain transfer need not occur when an association (CTC) brings about stabilization of the labile hydrogen atom. It is possible the results may also be attributed to a very high rate of copolymerization compared to chain-transfer processes. Intrinsic viscosity values of 0.080–0.112 dl/g, measured in DMF at 30°C, tend to support the initial suggestion since the molecular weights remained practically constant for varying monomer feed compositions. All the copolymers exhibited good thermal stability with decomposition beginning at approximately 300°C.

Assuming that the reaction was strongly influenced by the presence of a CTC, a series of experiments were carried out in which the MA and initiator concentrations were held constant and the concentration of 2-vinyl-1,3-dioxane **26** was varied (Fig. 10-2). As indicated by the curves in Fig. 10-2, the rate increases when the concentration of the allylic component increases, giving some support to participation of the CTC in the copolymerization mechanism.<sup>(130)</sup>



**27**

- A** R<sub>1</sub> = H, R<sub>2</sub> = CH<sub>3</sub>, R<sub>3</sub> = H, R<sub>4</sub> = H
- B** R<sub>1</sub> = H, R<sub>2</sub> = CH<sub>3</sub>, R<sub>3</sub> = H, R<sub>4</sub> = CH<sub>3</sub>
- C** R<sub>1</sub> = H, R<sub>2</sub> = CH<sub>3</sub>, R<sub>3</sub> = CH<sub>3</sub>, R<sub>4</sub> = H
- D** R<sub>1</sub> = C<sub>6</sub>H<sub>5</sub>, R<sub>2</sub> = H, R<sub>3</sub> = H, R<sub>4</sub> = CH<sub>3</sub>

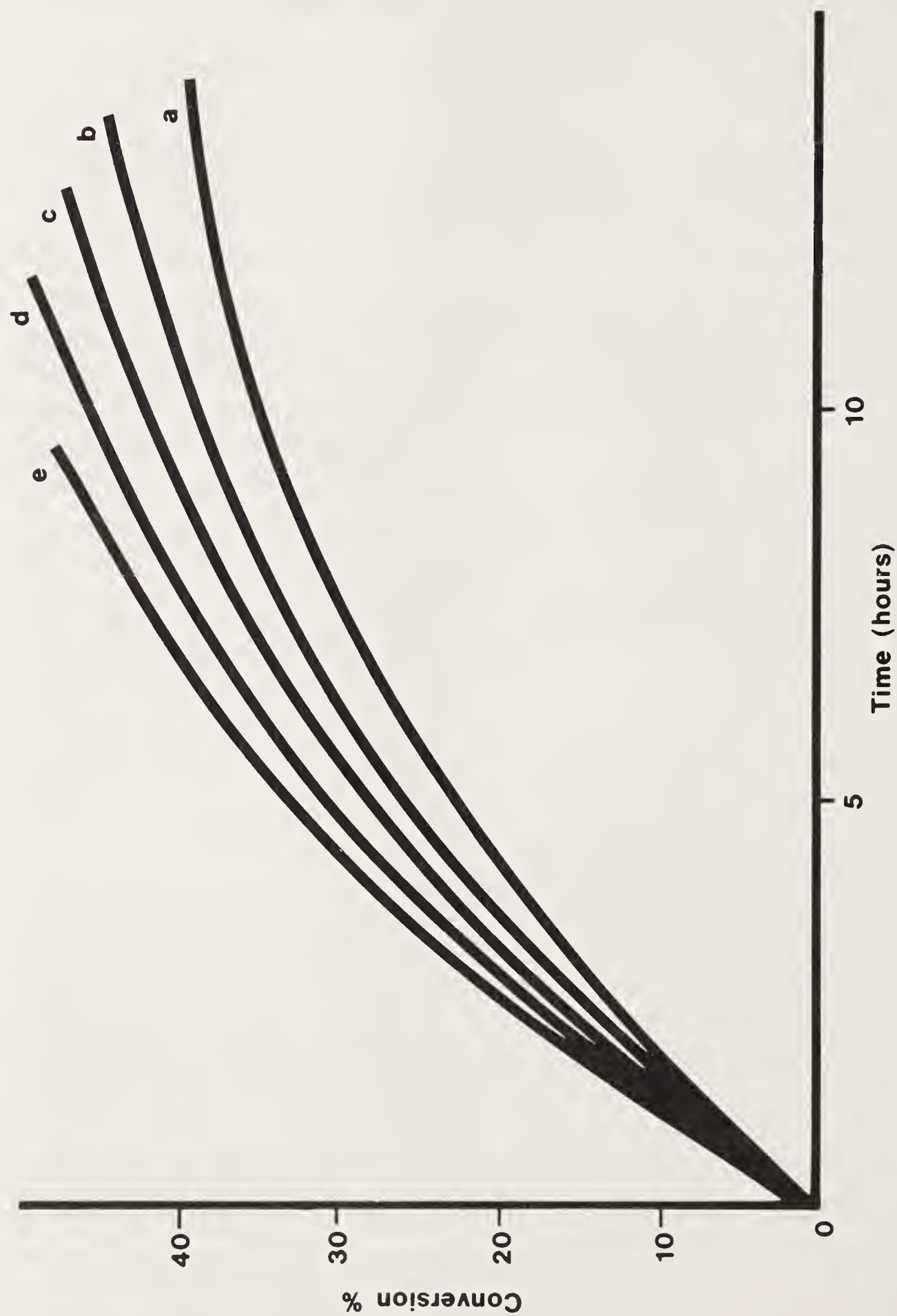


Fig. 10-2. Variation in the copolymerization rate for the 2-vinyl-1,3-dioxane-MA system when increasing the concentration of the allylic component.<sup>(130,132)</sup> Concentrations: a = 0.53; b = 0.70; c = 0.91; d = 1.14; e = 1.45 mole/liter of **26**.

Several isopropenyl and styryl derivatives of 1,3-dioxane **27**, i.e., 2-isopropenyl-1,3-dioxane **27A**, 2-isopropenyl-4-methyl-1,3-dioxane **27B**, 2-isopropenyl-5,5-dimethyl-1,3-dioxane **27C**, and 2-styryl-4-methyl-1,3-dioxane **27D** also readily form alternating copolymers with MA.<sup>(133,134)</sup> In the absence of initiator the monomers form Diels–Alder adducts (see Chapter 4) with the anhydride.

Solution copolymerization of 1,3-dioxane monomers **27A–27D** with MA were carried out over the temperature range of 50–90°C with different AIBN and comonomer concentrations.<sup>(133,134)</sup> The reactivity of the monomers with MA decreased in the order: **27A** > **27B** > **27C** > **27D**. For all four monomers, the copolymerization rates were maximum when equivalent amounts of monomer were present and first order with respect to the initial monomer concentrations. It was also observed that the rate of polymerization ( $R_p$ ) showed a square-root dependence on the initiator concentration, suggesting the presence of a bimolecular termination step. From these facts, a simplified rate expression was derived:

$$R_p = k(M)I^{1/2}$$

where M is **27**–MA and  $I$  is AIBN.

Conversions increased with time, in all four cases, and the monomer reactivity ratios (Table 10.3) decreased through the series. The low molecular weight of all four copolymers, as shown by intrinsic viscosity values, remained almost constant and independent of conversion. The constant production of only low-molecular-weight copolymer is probably achieved by very pronounced chain transfer to monomer or to CTC and low concentration of CTC during the course of the reaction.

The temperature dependence of the copolymerization rates were examined over the range 40–90°C. The results were plotted using the Arrhenius equation to give the activation energies  $E_R$  shown in Table 10.3.

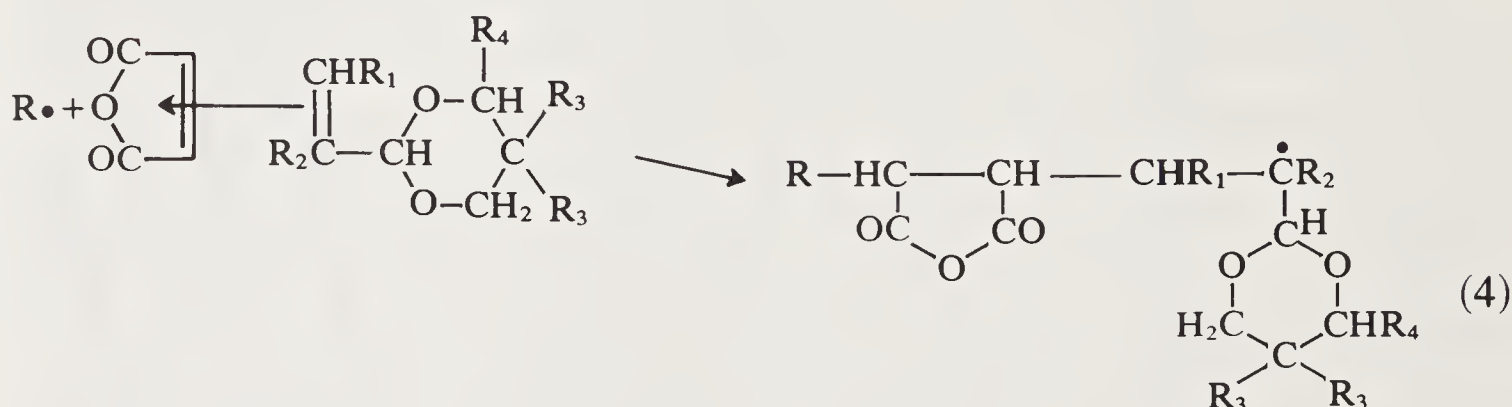
Table 10.3. Isopropenyl Dioxane–MA Copolymerization Activation Energy and Reactivity Ratios<sup>a</sup>

Copolymer	Solvent	Temperature range for $E_R$ (°C)	$E_R$ (kcal/mol)	$r_1^b$	$r_2$	$r_1r_2$
<b>27A</b> –MA	CH <sub>2</sub> ClCH <sub>2</sub> Cl	40–70	18.8	0.081	0.037	0.000 3
<b>27B</b> –MA	CH <sub>2</sub> ClCH <sub>2</sub> Cl	50–75	18.7	0.009	0.004	0.000 04
<b>27C</b> –MA	CH <sub>2</sub> ClCH <sub>2</sub> Cl	55–75	23.4	0.001 4	0.01	0.000 01
<b>27D</b> –MA	C <sub>6</sub> H <sub>6</sub>	60–90	13.3	0.09	0.09	0.008

<sup>a</sup> After Reference 134. By permission of John Wiley & Sons, Inc., New York, New York.  
<sup>b</sup> Values determined at 50, 60, and 80°C, respectively, from top to bottom in the table. Reactivity ratios recorded in the table in the appendix to Chapter 9.

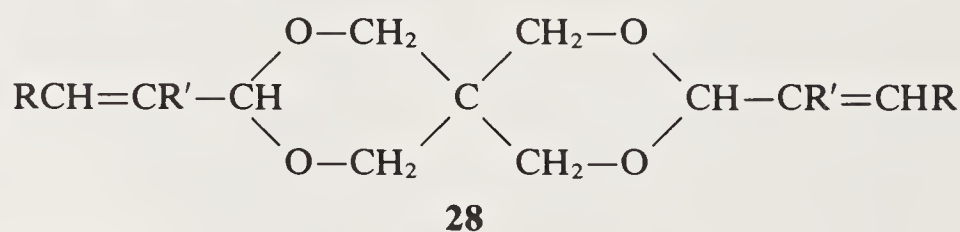


Nuclear magnetic resonance determinations showed the various (27A–27C)–MA charge-transfer complexes exhibited fairly high equilibrium constants,  $K_{eq} = 0.18\text{--}1.27$  liter/mole. Considering this, the equimolar compositions of the copolymers, and all other results, a mechanism for the free-radical-initiated copolymerization of 27A–27D with MA was conceived<sup>(134)</sup> [Eq. (4)]:



As shown in Eq. (4), the propagation mechanism is considered to be homopolymerization of the CTC.

The condensation product from acrolein and pentaerythritol, 28A, i.e., divinylspirobis-(*m*-dioxane) or diallylidenepentaerythritol, has been copolymerized with MA under a variety of conditions.<sup>(136)</sup> At low conversions, using BPO initiator, soluble alternating copolymers are produced.



- A**  $R = H, R' = H$   
**B**  $R = H, R' = CH_3$   
**C**  $R = CH_3, R' = H$

The  $\alpha\alpha$ - and  $\beta\beta'$ -monomers, i.e., dimethallylidenepentaerythritol 28B and dicrotyllidenepentaerythritol 28C, under the same free-radical-initiated copolymerization conditions, also give copolymers with MA. Copolymerizations must be carried to low conversion to get soluble copolymers. In all three cases, the maximum rates of copolymerization occurred at a monomer mixture ratio of (28A–28C)/MA of 0.5. Copolymer compositions and IR and NMR studies indicated that 1 : 1 copolymerization was achieved between each vinyl residue and MA.<sup>(136)</sup>

#### 10.2.6. Vinyl Esters

From the possible large family of vinyl esters, only vinyl acetate–MA copolymerization and copolymer has received significant study. Vinyl acetate–

MA copolymers, patented in 1936,<sup>(58)</sup> were marketed for some time by Monsanto Corporation as part of their Lytron resin series.<sup>(138,139)</sup>

As early as 1949, it was reported that vinyl acetate forms alternating copolymers with MA.<sup>(140,141,723)</sup> The heat of copolymerization ( $-\Delta H_{\text{cop}}$ ) or activation energy for the reaction is estimated to be 20.2 kcal/mol.<sup>(504)</sup> Melville and Burnett<sup>(233)</sup> estimated the copolymerization rate constant for the reaction, at 25°C, as  $1.8 \times 10^4 \text{ liters mol}^{-1} \text{ s}^{-1}$ . When the copolymerizations were run with excess vinyl acetate, it was discovered that the copolymerization progressed preferentially in a 1:1 fashion until all the MA was exhausted and then the residual vinyl acetate homopolymerized. Diethyl fumarate and diethyl maleate also undergo 1:1 copolymerization with vinyl acetate, with a  $-\Delta H_{\text{cop}}$ , respectively, of 18.6 and 20.0 kcal/mol.<sup>(140)</sup>

Others have also shown that vinyl acetate is capable of forming alternating copolymers with MA.<sup>(60,142-153)</sup> Imoto and Horiuchi<sup>(144)</sup> found that the greatest rate of copolymerization occurs at equimolar mixtures of the two monomers, giving under these conditions an 83% yield of alternating material in only 1-h polymerization.

The UV-initiated copolymerization of the monomer pair, in the absence of a photoinitiator, has received some study.<sup>(1021)</sup> In the case of high concentrations of MA in the feed, the copolymerization of the vinyl acetate-MA and styrene-MA pairs were comparable. The degree of polymerization ( $\overline{\text{DP}}$ ) decreased with increasing MA concentration.

By analogy with vinyl ethers, vinyl acetate-MA mixtures will also spontaneously copolymerize in the presence of the trioctylaluminum-MA complex (**9**, Sec. 10.2.2).<sup>(57,154)</sup>

Several authors feel that the CTC plays a strong role in the vinyl acetate-MA copolymerization.<sup>(151-153)</sup> However, others have shown that the maximum rate of copolymerization of the vinyl acetate-MA mixture need not occur at a 1:1 feed. Above 90°C, no CTC is detectable and vinyl acetate-MA copolymerization gives random copolymer.<sup>(155,156)</sup>

The patent literature<sup>(157-159)</sup> describes how vinyl acetate-MA copolymers may be prepared both in bulk and solution. Bulk copolymerization may be achieved with BPO at 60–80°C and the copolymer purified by precipitation with benzene from acetone solution, to give a hard, brittle material.<sup>(157)</sup> A vinyl acetate-peroxide mixture may be added to a toluene solution of MA at 80°C.<sup>(158)</sup> The precipitated product may be purified by several techniques.

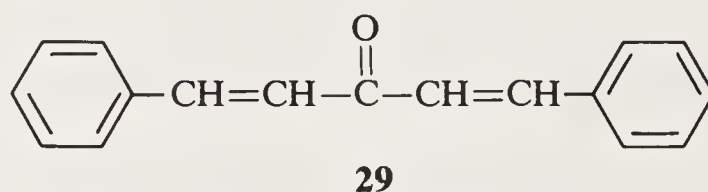
Isopropenyl acetate also readily forms alternating copolymers with MA.<sup>(140,143)</sup> The maximum heat of copolymerization,  $-\Delta H_{\text{cop}} = 17.8 \text{ kcal/mol}$ , for the system occurs at a 1:1 monomer mixture.<sup>(140,143)</sup> In contrast to vinyl acetate, isopropenyl acetate does not homopolymerize in mixtures with MA and only copolymer is obtained even in the presence of a large excess of isopropenyl acetate.<sup>(140)</sup>



### 10.2.7. Vinyl Ketones

Very little effort has been devoted to studying the copolymerization of vinyl ketone monomers with MA. An alternating mechanism has been claimed for the copolymerization of vinyl cyclohexyl ketone with MA.<sup>(160)</sup> The constancy of the 1:1 monomer ratio in the copolymer, regardless of monomer feed, and the observation that the maximum rate of copolymerization occurs at equimolar monomer feed was cited as support for the CTC polymerization mechanism. The reactivity ratios (see Chapter 9),  $r_1(\text{MA}) = 0.013$  and  $r_2(\text{vinyl cyclohexyl ketone}) = 0.046$ , plus the  $Q = 0.045$  and  $e = 0.53$  values for vinyl cyclohexyl ketone, clearly shows that this comonomer should prefer to undergo alternating copolymerization with MA.<sup>(160)</sup>

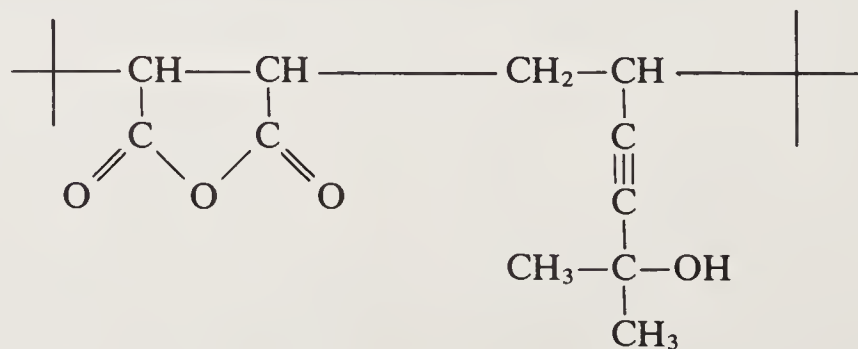
Dibenzalacetone **29**, a  $\beta,\beta'$ -diphenyl ketone, has also been reported to form copolymer with MA.<sup>(161)</sup>



When equimolar amounts of the two monomers are heated in benzene for 24 h at 100°C, with 1.3% by weight of *tert*-butyl peroxide, copolymer **29**-MA is obtained in an 85% yield. Using the same conditions but varying the monomer ratios and carrying out the copolymerizations to low conversions, it was shown that, regardless of the monomer feed ratio, a 1:1 alternating copolymer was obtained.<sup>(161)</sup>

### 10.2.8. Acetylene-Type Monomers

Copolymerization of substituted acetylenes with MA has received sparse attention. Only phenylacetylene<sup>(162-165)</sup> and *p*-dimethylamino-phenylacetylene<sup>(166)</sup> copolymerizations have been studied. Copolymers based on dimethylvinyl-ethynyl-carbinol have also been briefly explored.<sup>(167)</sup> Copolymerization occurred at the vinyl group, giving an alternating copolymer with anhydride and pendent ethynyl-carbinol residues **30**.



**30**



Copolymerization of phenylacetylene with MA have been achieved with both  $\gamma$  radiation<sup>(162)</sup> and free-radical initiation.<sup>(163)</sup> Using  $\gamma$  radiation, the highest conversion was obtained for a phenylacetylene:MA ratio of 1:2 (versus 1:1 and 3:1) and yields increased with dose (42–1 012 rads/s). When polymerized in dioxane with free-radical initiators, the rate was 0.83 with respect to initiator and independent of monomer concentration.<sup>(163)</sup> When heated at 98°C for 6.5 h copolymer of high molecular weight (up to  $10^5$ ) was obtained.<sup>(164)</sup> Studies on photochemically initiated polymerizations resulted in the relationship  $[\eta] = 6.5 \times 10^{-3} \bar{M}_n^{0.80} \text{ cm}^3/\text{g}$  (acetophenone, 29.6°C).<sup>(164)</sup> It is doubtful, based on other efforts,<sup>(165)</sup> that alternating copolymer is produced. The material most probably contains some poly(phenylacetylene) blocks. Since MA forms a CTC with poly(phenylacetylene) and copolymerization of the two materials can occur, the product from phenylacetylene–MA copolymerization could have a very complex structure.<sup>(168)</sup>

For *p*-dimethylaminophenylacetylene, various monomer mixtures were found to undergo thermal polymerization to produce, in each case, a copolymer having a 2:1 molar ratio of MA:*p*-dimethylaminophenylacetylene. Studies showed that both types of copolymers exhibited paramagnetic properties.

### 10.2.9. Vinyl Heterocyclics

A variety of heterocyclic compounds with vinyl residues, such as *N*-vinylpyrrolidone,<sup>(169–172)</sup> *N*-vinylcarbazole,<sup>(173,174)</sup> *N*-vinylphthalimide,<sup>(171,175)</sup> *N*-vinylsuccinimide,<sup>(171,177,178)</sup> *N*-vinylcaprolactam,<sup>(179)</sup> and vinylenecarbonate<sup>(80)</sup> readily copolymerize with MA to give equimolar copolymer. *N*-Vinylcarbazole is also known to undergo free-radical-initiated equimolar copolymerization with diethyl fumarate and fumaronitrile.<sup>(558)</sup> Vinyl and isopropenyl substituted pyridines,<sup>(118,181)</sup> thiazole, benzoxazole, and quinolines<sup>(118)</sup> also copolymerize with MA. To what extent these copolymerizations tend to go equimolar has not been explored.

When mixtures of *N*-vinylpyrrolidone (NVP) and MA are exposed to ultraviolet radiation, the solution turns from yellow to pink and then to scarlet, giving good yields of alternating copolymer in only 3 h at 30°C.<sup>(170)</sup> The 1:1 CTC of NVP–MA is known to initiate the thermal and photopolymerization of methyl methacrylate.<sup>(169)</sup>

Using AIBN initiator and bulk copolymerization at 65°C, copolymers are produced with strictly alternating (1:1) composition, regardless of the initial monomer mixture of *N*-vinyl monomer and MA.<sup>(182)</sup> For example, the copolymer of MA and NVP contained 6.75% *N* (theoretical % for a 1:1 is 6.70% *N*). Similar results were observed for the MA–*N*-vinylsuccinimide (NVS) and MA–*N*-vinylphthalimide (VP) systems. Investigation of the compositions of the products, formed in the cases for high conversions (40–100%)

and nonequimolar starting mixtures, indicated that both alternating copolymerization and homopolymerization of the *N*-vinyl monomer may occur. Furukawa *et al.*<sup>(178)</sup> recently showed that NVS–MA mixtures could be copolymerized at 60°C with free-radical initiation to produce alternating polymer with inherent viscosities, measured in dimethylsulfoxide at 50°C, as high as 0.82 dl/g. If MA is used in excess, it may be separated unchanged and only copolymer is formed.

Since the equilibrium constants for the various *N*-vinyl–MA charge-transfer complexes are fairly high (see table in the appendix to this chapter), it has been suggested that there is a good chance that these charge-transfer complexes are playing a major role in the copolymerization mechanism. It is assumed that a CTC would attach to a polymer radical more preferentially than any of the starting *N*-vinyl monomers, since the combination of two monomers in a CTC should contribute to a reaction with a high preexponential multiplier.<sup>(182)</sup>

Analysis of the polymerization of charge-transfer complexes of MA with NVP and NVS has been explored by the method of invariant transformations.<sup>(172)</sup> Kinetics of the various polymerizations were represented by a single invariant curve. The invariance concerned temperature, initiator concentration, chemical structure, concentration of the monomer, and degree of CTC interaction. In contrast to the concept in the previous paragraph, this lends support to a “common” polymerization mechanism for these systems. Hydrolysis of these copolymers provides potentially useful alternating polyampholytes.<sup>(177)</sup>

Mixtures of *N*-vinyl- $\epsilon$ -caprolactam with MA undergo spontaneous copolymerization to give alternating copolymer.<sup>(179)</sup> Using BPO initiator, DMF solvent, and a polymerization temperature of 70°C, maximum rates were observed at a 1 : 1 monomer feed. The activation energy for the system is 13.0 kcal/mol, compared to 16.0 kcal/mol reported for alternative copolymerization of styrene.<sup>(293,295)</sup> Intrinsic viscosities  $[\eta]$  of the copolymer could be calculated by the relationship

$$[\eta] = \eta_{sp}/[C(1 + 0.333\eta_{sp})],$$

where  $\eta_{sp}$  is the specific viscosity and  $C$  is the concentration in g/cm<sup>3</sup>. The highest intrinsic viscosity (7.11 dl/g), determined in DMF (0.2 g/100 ml, 25°C), was observed for equimolar feed copolymerization.

Very recently the 1-vinylindole, 2-methyl-1-vinylindole, 3-methyl-1-vinylindole, 2,3-dimethyl-1-vinylindole,<sup>(183)</sup> 2-methyl-1-vinylimidazole<sup>(1071)</sup> and 1-vinylimidazole<sup>(1138)</sup> copolymerizations with MA have been studied. The molecular structure of the 1-vinylindole–MA copolymer, as shown by NMR, was complicated by the formation of indoline rings along the chains by an attack of the propagating anhydride radical at the 2 position of the indole ring. Only the 2,3-dimethyl-1-vinylindole monomer copolymerized in a 1 : 1



alternating fashion with MA. The structure and properties of the copolymers formed from the spontaneous copolymerization of the 2-methyl-1-vinylimidazole with MA have not been studied. The monomer *n*-vinylindole is also reported to undergo free-radical-initiated equimolar copolymerization with diethyl fumarate.<sup>(537)</sup> It has also been reported that 1-vinylimidazole, with  $Q = 0.1$ , copolymerizes in a 1 : 1 fashion with monomethyl maleate.<sup>(1138)</sup>

#### 10.2.10. Olefin Monomers

Olefin-MA copolymerizations have received considerable study. The lower  $\alpha$ -olefins are known to copolymerize more easily with MA than the higher  $\alpha$ -olefins, to produce equimolar copolymers. Procedures are also known for preparing nonequimolar copolymers (see Chapter 9). Copolymer products are available commercially from olefins up to 18 carbon atoms. For example, Monsanto has for some time marketed ethylene-MA (EMA) copolymers and Gulf Corporation now markets a polyanhydride from a  $C_{18}$   $\alpha$ -olefin. These copolymers are usually available in both solid and solution form, at several viscosity grades.

Using a variety of solvents and initiators<sup>(23,184-186)</sup> or  $\gamma$  radiation,<sup>(189)</sup> ethylene copolymerizes with MA to give alternating 1 : 1 copolymers, independent of monomer feed ratios. For copolymerizations run in benzene from 4 to 40 atm and using BPO initiator, the inherent viscosity of the resulting copolymers are proportional to the ethylene concentration.<sup>(185)</sup> At 40 atm, the overall activation energy, over the range 45–73°C, was estimated to be  $25 \pm 2$  kcal/mol.<sup>(185)</sup> Regardless of the ethylene concentration, from 0.5 to 60 mol % in the reaction mixture, alternating copolymers were obtained and the maximum rate of copolymerization occurred at a 1 : 1 monomer feed mixture.<sup>(186)</sup> Rates of copolymerization are generally greater in benzene or ketone solvents than under bulk conditions. Over the temperature range 70–130°C, the molecular weights decrease with temperature rise and increase of MA concentration in monomer feed.<sup>(186)</sup> As pressure increases molecular weights generally increase. A good laboratory procedure for the preparation of ethylene-co-MA polymers has been published.<sup>(188)</sup>

Machi *et al.*<sup>(189)</sup> studied the mechanism of the ethylene-MA copolymerization by preparing 1 : 1 copolymers at low conversion, using  $\gamma$ -ray initiation ( $^{60}\text{Co}$  source) as well as AIBN or diisopropyl peroxydicarbonate. The products were essentially the same, regardless of the method of initiation. In the  $\gamma$ -ray process, the rates of copolymerization, as indicated by the copolymer viscosities, were proportional to the fraction of olefin in the charge and independent of MA, provided that ethylene was present in excess. The rate-determining step is the addition of ethylene to a MA unit at the growing chain end. In this case, the radiogenic process activation energy was estimated at 1.8 kcal/mol, compared with 27.5 kcal/mol for the AIBN process. Machi



*et al.*<sup>(189)</sup> claim the large difference is due mainly to the energy required for heterolytic dissociation of the AIBN.

It is interesting to note here that alternating ethylene-co-MA polymer after esterification with methyl alcohol is head-to-head poly(methyl acrylate),<sup>(199,200,520,1072)</sup> which cannot be prepared by conventional techniques. With the exception of glass transition ( $T_g$ ) temperatures, the alternating ethylene-co-maleic ester copolymer is comparable to poly(methyl acrylate). The head-to-head polymer  $T_g$  is higher than the conventional head-to-tail poly(methyl acrylate).

A host of patents are available concerning the preparation and use of  $\alpha$ -olefin-MA copolymers. Procedures are claimed for preparing ethylene-MA in toluene or xylene in the presence of BPO at 85–100°C and pressures of 860–950 atm.<sup>(190)</sup> The white, solid product precipitates from solution, as formed. Low-molecular-weight products are readily prepared in ethylene dichloride with butyraldehyde chain-transfer agent.<sup>(191)</sup> A bulk process, using molten MA, acetyl peroxide initiator, and dodecyl mercaptan chain-transfer agent, is described.<sup>(192)</sup>

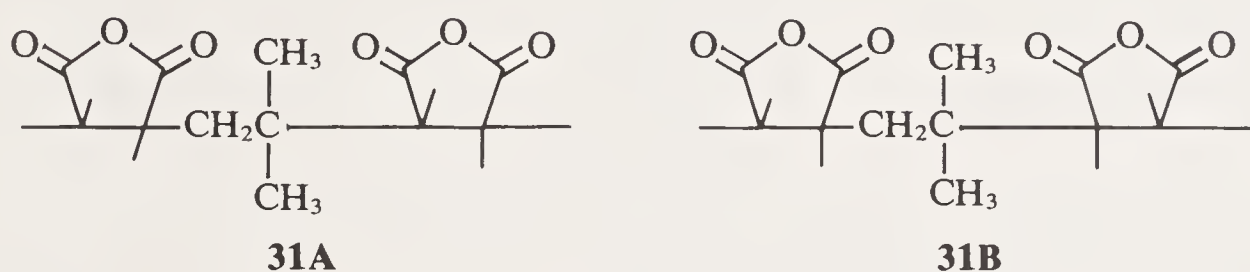
Using benzene solvent and a variety of initiators, Frank<sup>(184)</sup> described the preparation and properties of  $\alpha$ -olefin-MA copolymers from propylene, 1-butene, isobutene, *cis*- and *trans*-2-butene, 2-methyl-1-pentene, 2,4,4-trimethyl-1-pentene, 1-hexene, and 1-octene. In order to characterize the materials, the  $[\eta]$ - $\bar{M}_w$  relationship was elucidated for the polymers:

$$[\eta] = 1.9 \times 10^{-4} \bar{M}_w^{0.66} \quad (2\text{-butanone, } 25^\circ\text{C})$$

Others have also looked at the copolymerization of  $\alpha$ -olefins with MA.<sup>(193–196)</sup> In general, all the copolymerizations produce copolymers containing 50 mol % olefin. A comparison of the yields obtained after 1–3 h at 70°C gives the following order of reactivity for the lower olefins: isobutene > propylene > ethylene > 1-butene. Higher olefins, such as 1-hexene, 1-octene, and 2,4,5-trimethylpentene (diisobutylene), gave only low-molecular-weight materials in low yields at 80°C. The monomer 2-methyl-1-pentene, in contrast, is almost as reactive as propylene and provides copolymers in an 80–85% yield after only 4–7 h. For six carbon  $\alpha$ -olefins, such as 1-hexene, solution copolymerization in dihalogenated aliphatic solvents, with standard free-radical initiators, work best to give conveniently isolated particulate copolymer.<sup>(196)</sup> For the butene series, the molecular weight of the alternating copolymers varied as follows, with isobutene giving the highest molecular weight: isobutene  $\gg$  *n*-butene > *cis*-butene  $\geq$  *trans*-butene.<sup>(194)</sup>

When equimolar parts of isobutene and MA are copolymerized in THF at 70°C, using BPO initiator, a 95% yield of alternating copolymer **31**, with specific viscosity of 0.28 dl/g (1 g/100 ml DMF, 25°C), is obtained.<sup>(195)</sup> In contrast, benzene solvent gave copolymer with inherent viscosity of 0.60 dl/g.

Nuclear magnetic resonance studies showed the methyl groups resonance was composed of four peaks of approximate equal intensity from 1.3 to 1 ppm, supporting *threo*-diisotactic **31A** and *threo*-disyndiotactic **31B** structures assigned to the copolymer.<sup>(195)</sup>



The suspension copolymerization of MA with  $\alpha$ -olefins, such as isobutylene and diisobutylene, can be accomplished in the presence of novel macromolecular dispersing agents, which are soluble in aliphatic hydrocarbons.<sup>(197)</sup> By this method the copolymers are received as finely divided powders with a relatively uniform particle size. For the MA–isobutylene or diisobutylene copolymers, an excess of the respective olefin is used as a dispersing medium and the dispersing agents, prepared by the chemical modification of various alternating copolymers of MA, permitted the preparation of the isobutylene and diisobutylene copolymers in high yields and with intrinsic viscosities in DMF (100 ml/g, 30°C), respectively, in the range 0.14–0.18 and 0.21–0.34 dl/g. Equimolar  $\alpha$ -olefin–MA copolymers may also be conveniently prepared in aliphatic hydrocarbon solvents, using a 0.02–5 parts by weight long-chain olefin ( $C > 20$ )–MA copolymer as a dispersant.<sup>(1041)</sup> The insoluble copolymers are readily collected as a finely divided powder. Other procedures have also been patented for obtaining  $\alpha$ -olefin–MA copolymers as fine powders.<sup>(1048)</sup>

The copolymerization of MA with propylene has also been studied in great detail.<sup>(184)</sup> With BPO (2% by weight) at 70°C, high-molecular-weight copolymer, with intrinsic viscosities in 2-butanone up to 0.55 dl/g, is formed in essentially quantitative yield within 3 h at 10 atm pressure. At 2 atm pressure, the yield dropped to only 12%. The most effective initiator was 2,4-dichlorobenzoyl peroxide. As little as 0.2–0.4 wt. % of this initiator provided a quantitative yield in only 2 h at 60–70°C, having intrinsic viscosity in 2-butanone of 0.38–0.61 dl/g. An oxidation–reduction initiator, composed of BPO and *p*-toluene-sulfinic acid is even more effective, giving a quantitative yield in only 1 h at 65°C. The same oxidation–reduction pair also works well with isobutylene, but not with ethylene or 2-methyl-1-pentene.<sup>(198)</sup> The molecular weight of the copolymer, as indicated by intrinsic viscosities in 2-butanone, increased with pressure, but decreased with increasing level of initiator or temperature.<sup>(184)</sup>

Bulk copolymerization of MA in excess liquid propylene has been conducted at 70°C, using lauroyl peroxide initiator. Excellent yield of the 1:1



Table 10.4. Viscosity–Molecular Weight Relationship for 1:1 MA–Olefin Copolymers<sup>a</sup>

Comonomer	Solvent (25°C)	Intrinsic viscosity [η]
Propylene <sup>b</sup>	2-Butanone	$1.9 \times 10^{-4} \bar{M}_w^{0.66}$
	γ-Butyrolactone	$2.0 \times 10^{-4} \bar{M}_w^{0.70}$
2-Methyl-1-pentene <sup>c</sup>	2-Butanone	$2.9 \times 10^{-4} \bar{M}_w^{0.83}$
	γ-Butyrolactone	$3.5 \times 10^{-4} \bar{M}_w^{0.83}$

<sup>a</sup> After Reference 184. By permission of Hüthig and Wepf Verlag, Basel, Switzerland.

<sup>b</sup> Molecular weight range for study 51 000–259 000.

<sup>c</sup> Molecular weight range for study 38 000–125 000.

alternating copolymer, with an intrinsic viscosity measured in 2-butanone (100 ml/g at 25°C) of 0.47 dl/g, is obtained in only 3 h.

Using intrinsic viscosity and light-scattering molecular weight data, viscosity molecular weight relationships have been derived for the 1:1 copolymers of MA–propylene or 2-methyl-1-pentene (Table 10.4).<sup>(184)</sup> Propylene–MA copolymers are colorless, amorphous solids that soften over the range 210–235°C. The materials may be molded to give glassy, somewhat brittle sheets. The copolymers are soluble in polar solvents, such as ketones, esters, and DMF and insoluble in nonpolar solvents, such as aliphatic and aromatic hydrocarbons. Solubility in nonpolar solvents increases as the olefin chain length grows.

Tanaka and Vogl<sup>(199)</sup> recently studied the copolymerization of *cis*-butene-2 with MA as a route to poly(methyl crotonate). Confirming the work of Otsu and coworkers,<sup>(193)</sup> alternating copolymers were obtained with specific viscosities in DMF (0.2 g/100 ml, 30°C) as high as 0.25 dl/g. Esterification of the copolymer with methyl alcohol produced head-to-head poly(methyl crotonate), not obtainable by convential techniques. Analogous to head-to-head poly(methyl acrylate), the head-to-head poly(methyl crotonate)  $T_g = 107\text{--}108^\circ\text{C}$  was significantly higher than the  $T_g$  for head-to-tail poly(methyl crotonate).<sup>(199,200)</sup>

The monomers, 4-cyclohexyl-1-butene, 4-phenyl-1-butene,<sup>(37,201)</sup> 5-phenyl-1-pentene,<sup>(37)</sup> 4-vinylepoxycyclohexane,<sup>(202)</sup> vinylcyclohexane,<sup>(203,204)</sup> and α-methylvinylcyclohexane,<sup>(203,204)</sup> have also received some attention in copolymerization studies with MA.

Bulk copolymerization of 4-phenylbutene-1 and 5-phenylpentene-1 with MA at 60°C, using AIBN, gave alternating copolymer as shown in Table 10.5. The copolymers were estimated to have molecular weights of the order of 20 000. In contrast, copolymerization of 4-phenylbutene-1 in 2-butanone at 70°C, with AIBN, gave in 5 h only a 21% yield of copolymer having a molecular weight of 2 000.



Table 10.5. Copolymers of MA with 4-Phenylbutene-1,5-Phenylpentene-1, and 3-Phenylpropene-1<sup>a</sup>

MA/olefin molar feed ratio	Time (h)	Mole % anhydride in copolymer	Yield (%)	Viscosity <sup>b</sup> $\eta$ (dl/g)
4-Phenylbutene-1				
1:2	—	49	—	—
1:1	3.0	48	24	0.15
2:1	—	48	—	—
5-Phenylpentene-1				
1:3	—	53	—	—
1:2	—	53	—	—
1:1	3.0	53	14	0.10
2:1	—	53	—	—
3:1	—	52	—	—
3-Phenylpropene-1	3.0	53	7	0.02

<sup>a</sup> Reprinted with permission from *J. Org. Chem.* **27**, 1201 (1962). Copyright © 1962, American Chemical Society.  
<sup>b</sup> Determined in DMF at 25°C.

Using both bulk and solution copolymerization techniques, 4-cyclohexyl-1-butene failed to produce copolymer with MA.<sup>(201)</sup> The difference between the reactivity of 4-phenyl and 4-cyclohexylbutene-1 with MA is not well understood. It is hard to believe that this difference in reactivity could be wholly ascribed to inductive effects, since both rings are separated from the double bond by two methylene residues. Charge-transfer complexes play a role in all mechanisms advanced to explain the observed phenomenon.<sup>(201)</sup>

Vinylcyclohexane and a-methylvinylcyclohexane, because of the ready formation of allyl-type radicals of low reactivity, do not polymerize in the presence of radical initiators. However, the two monomers will undergo equimolar copolymerization with MA in the presence of free-radical initiators.<sup>(203,204)</sup> Alternating copolymerization is attributed to a radical-coordination mechanism, brought about by a weak intermolecular interaction occurring in formation of a CTC in the two systems. An increase in the donor-acceptor activity of the monomers in changing from vinylcyclohexane to a-methylvinyl-cyclohexane is accomplished by an increase in the rate of copolymerization with MA, tending to confirm the formation of a CTC in the propagating mechanism. An increase in CTC interaction, on going from vinylcyclohexane to a-methylvinylcyclohexane, functions to give a greater tendency for alternation of the two monomer residues. For both cases, the overall energy of activation was estimated at 20.4 kcal/mol,<sup>(203)</sup> despite difference in donor properties between the two monomers.

The low-molecular-weight ( $\bar{M}_n = 3\,000$ ) vinylcyclohexane-MA copolymers are slightly colored, amorphous powders that are soluble in a number of organic solvents. The materials start to decompose at 250°C. Maleic anhydride will also undergo alternating copolymerization with 2-vinylbicyclo[2.2.1]heptane.<sup>(205)</sup> Bulk copolymerization of equimolar amounts of the two monomers with AIBN for 18 h at 60°C gave a 19% yield of low-molecular-weight copolymer. Increasing the amount of 2-vinylbicyclo[2.2.1]heptane in the monomer mixture does not appear to decrease the copolymerization rate. The  $Q = 0.025$  and  $e = 0.45$  values of 2-vinylbicyclo[2.2.1]heptane shows this monomer should readily undergo alternating copolymerization with MA.

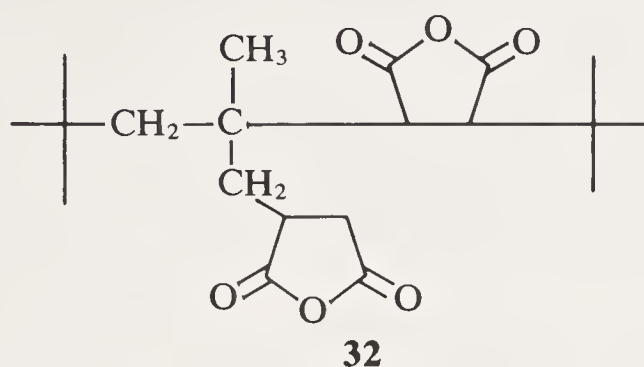
The effect of high pressure on the copolymerization and terpolymerization of MA with substituted ethylenes and cyclic olefins has recently been critically examined by Kellou and Jenner.<sup>(187,1075,1135)</sup> Copolymerization of 1-hexene, 2-ethyl-1-hexene, 2-methyl-2-butene(trimethylethylene), and 2,3-dimethyl-2-butene(tetramethylethylene) were run in chloroform at 70–90°C with lauroyl peroxide. The pressure was varied from 1 bar to 3 kbars. The pressure effect on the rate of copolymerization was found to be considerable, leading to high negative values of the activation volume, especially when the olefin comonomer was crowded with bulky substituents. Polymer composition did not vary significantly with pressure, i.e., the copolymers remained alternating, and the reactivity ratios were found to be less affected by pressure than rates and generally decreased slightly with increasing pressure. Pressure also influences the  $e$  value of the monomers. Contrary to a previous report,<sup>(187,232)</sup> the copolymerization of tetramethylethylene with MA is shown to proceed in the normal manner; i.e., the rate of copolymerization goes up with pressure.

The synthesis and stereochemistry of alternating copolymers of MA with chiral  $\alpha$ -olefins, using 1-heptene, 2-methyl-1-butene, etc., showed that polymer yield depended on the position of side-chain branching.<sup>(1143)</sup> Lowest yields were obtained when methyl branching was in the  $\alpha$ -position to the double bond. All copolymers showed rotary power of the same sign as the corresponding  $\alpha$ -olefin homopolymer, although the intensity was markedly lower, indicating atacticity. It was shown chirality was induced into the copolymer MA moieties.

Allyl, butenyl, and isobutenylsuccinic anhydride (see Chapter 6) will undergo free-radical-initiated copolymerization with MA and maleimides, to give low-molecular-weight, equimolar copolymers.<sup>(46)</sup> The MA copolymerizations were studied both neat and in a variety of solvents, using AIBN, di-*tert*-butyl peroxide, etc., initiators, over the temperature range 75–144°C. Elemental data showed the copolymers to be essentially equimolar, regardless of the starting monomer feed ratios. The rates of conversion tended to be highest for polymerization of 1 : 1 mixtures. The relative reactivities, measured by percent conversion under comparable copolymerization conditions, were



isobutenylsuccinic > allylsuccinic > butenylsuccinic anhydride. The structure of the water-soluble isobutenylsuccinic anhydride-MA copolymer **32**, prepared in >60% yield by using di-*tert*-butyl peroxide initiator at 133–136°C for 6 h in a xylene solvent mixture, is shown below.



### 10.2.11. Diolefin Monomers

Diolefins, such as butadiene, isoprene, substituted butadienes, 2,4-hexadiene, 1,3-pentadiene, and 1,4-pentadiene, are all known to undergo free-radical-initiated copolymerization with MA. In the absence of initiators, the well-known diene-dienophile reaction can occur to give Diels-Alder products (see Chapter 4). It has also been claimed that it is possible to prepare butadiene-MA copolymers with Ziegler-type catalysts (see Chapter 9).<sup>(206)</sup>

Butadiene copolymerizes with MA to give an alternating copolymer high in *cis*-1,4 microstructure.<sup>(207–210)</sup> This is in sharp contrast to conventional free-radical-initiated polymerization of butadiene which is known to give homopolymer rich in *trans*-1,4 microstructure. Mixtures of the two monomers are readily copolymerized by AIBN,<sup>(207)</sup> *tert*-butyl peroxyphthalate, or by a solvent which forms a peroxide, i.e., oxygenated dioxane.<sup>(209)</sup> Copolymer yields generally increase with decreasing initiator half-life or initiator concentration. In general, best results are usually obtained by charging the highest level of initiator commensurate with keeping the rather violent reaction under control. Molecular weights of the materials drop with increasing temperature or increasing initiator concentration.

In all cases, the copolymers are essentially equimolar regardless of the composition of the monomer feed, and the various copolymerization conditions serve only to cause variations of the copolymer microstructure. For example, the infrared spectrum of a copolymer prepared at 80°C, using *t*-butyl peroxyphthalate in cyclohexanone solvent, showed approximately 85–90% *cis*-1,4 units.<sup>(210)</sup> In contrast, the infrared spectrum of a copolymer prepared in benzene solvent at 60°C with AIBN has approximately 74% *cis*-1,4 units. A homopolymer of butadiene, prepared under the same conditions, has approximately 62% *trans*-1,4 residues.<sup>(207)</sup>

It is known that butadiene exists mainly in the *trans* structure and ordinary free-radical polymerizations and copolymerizations produce polymers that



have *trans*-1,4 microstructure and a little 1,2- and *cis*-1,4 residues. It is assumed that MA forms a CTC with the butadiene to give a cisoid intermediate that participates in the polymerization mechanism to produce copolymer high in *cis*-1,4 microstructure. Several claim there is strong evidence for butadiene–MA CTC participation in the copolymerization mechanism.<sup>(207–210)</sup> As evidence, they point out that it is well known that the CTC type of interaction is strongest in the case of *cis* overlapping through the transition state, similar to that in the Diels–Alder reaction (see Chapter 4) of butadiene.<sup>(211)</sup>

Isoprene–MA copolymerizations have also received substantial study by Gaylord and coworkers.<sup>(113,208–210,212,214)</sup> Copolymerizations have been accomplished with this monomer pair using several different free-radical initiators and a variety of solvents at different temperatures. Using *t*-butyl peroxyvalate initiator and copolymerizing an equimolar mixture of the two monomers in cyclohexanone at 80°C gave >70% conversion to a 1 : 1 alternating copolymer. These copolymers are also high in *cis*-1,4 microstructure.<sup>(113)</sup>

Isoprene will also copolymerize with MA using ultraviolet light (253 Å) and photosensitizers.<sup>(113)</sup> Yields are best for the 1 : 1 alternating copolymers when the photosensitizer has a triplet energy >74 kcal/mol.

In summary, the production of alternating MA copolymers from butadiene and isoprene progresses best by using initiators with short half-lives, preferably less than 60 min at 100°C, as illustrated in Table 10.6 with isoprene monomer.

Diene–MA copolymerizations proceed best in polar solvents, such as dioxane, cyclohexanone, or THF. These solvents hasten the decomposition of the initiators. Also, copolymerization in polar solvents proceeded in a homogeneous fashion and gave higher-molecular-weight materials. The soluble copolymers are easily isolated by precipitation with benzene. In contrast, copolymerizations run in xylene or toluene yield crosslinked (pop-

Table 10.6. Copolymers of Isoprene and MA<sup>a</sup>

Initiator <sup>b</sup>	Half-life at 100°C (min)	Yield (%)
<i>t</i> -Butyl hydroperoxide	165	<2
Dicumyl peroxide	100	7
Benzoyl peroxide	0.4	19
Azobisisobutyronitrile	0.1	30 <sup>c</sup>

<sup>a</sup> Reprinted from Reference 208, p. 873, by courtesy of Marcel Dekker, Inc., New York, New York.

<sup>b</sup> All copolymerizations (1 : 1 monomer mixtures) run in dioxane at 100°C.

<sup>c</sup>  $[\eta] = 0.15$  dl/g (cyclohexanone, 25°C). Depending on reaction conditions, i.e., solvent, temperature, and initiator,  $[\eta]$  may vary from 0.2 to 0.8 dl/g.<sup>(208,210)</sup>

corn)polymeric materials and copolymerization rates are retarded.<sup>(214)</sup> Gaylord<sup>(208)</sup> suggests the rates are retarded because the aromatic hydrocarbons compete with the diene in forming charge-transfer complexes with MA.

Composition studies for both systems show equimolar incorporation of the various comonomers, even when a large excess of butadiene or isoprene is charged. The small amount of Diels–Alder product (see Chapter 4) usually formed during the copolymerization is easily extracted.<sup>(215,1023)</sup> In both cases, the molecular weight of the product decreases with increasing reaction temperature. Infrared spectroscopy clearly shows that, for both cases, the configuration of the unsaturated residues in the chains are 75–95% *cis*-1,4, 5–20% *trans*-1,4, and 0–5% 1,2-vinyl.

Copolymerization of butadiene and isoprene with monobutyl maleate and dialkyl maleates or fumarates is also reported to give equimolar copolymer.<sup>(534,541,544,831)</sup> The copolymerizations were initiated by UV radiation,<sup>(534)</sup> electric current,<sup>(541)</sup> and conventional free-radical<sup>(544)</sup> initiators. Copolymerization is believed to occur by *cis*-1,4 addition, which is explained by participation of a CTC.

The alternating copolymerization of MA with 2,3-dimethylbutadiene has been examined in great detail.<sup>(28,216,217)</sup> Copolymerizations were initiated by both photochemical decomposition of AIBN and irradiation by  $\gamma$  (<sup>60</sup>Co) rays. In all experiments, the compositions of the copolymers were essentially the same and did not differ from equimolar composition, within limits of error. As usual, rates of copolymerization were maximum at equimolar ratio of monomers. These results, the fact that the reactivity ratios appeared to be zero for the system (see table in appendix to Chapter 9), and the fact that mixtures of the two monomers formed yellow solutions are very typical for most of the copolymerizations that give alternating copolymers. Free-radical copolymerization of the monomer pair is considerably altered by CTC forming compounds such as diethyl aluminum chloride and zinc chloride.<sup>(217)</sup> These agents participate in the formation of the intermediate reaction charge-transfer complexes and bring about production of nonequimolar copolymer.

To better understand the mechanism of the dimethylbutadiene–MA copolymerization, low-temperature (–196 to –60°C) initiated polymerizations were studied with  $\gamma$  rays and spectral changes observed by electron spin resonance.<sup>(216)</sup> The study shows that liquid-phase copolymerization of MA and dimethylbutadiene takes place with the formation of a copolymer with regular alternation of monomer units, even while heating a glassy monomer mixture exposed to  $\gamma$  radiation at –196°C. From an analysis of the electron paramagnetic resonance spectra and calorimetric data, it was clearly established that the mechanism of copolymerization for this system consists of the stepwise addition of monomer molecules to a growing radical. This is contrary to a CTC homopolymerization model proposed earlier.<sup>(218)</sup> It is assumed that the cause of the almost exclusive addition of monomers to “foreign” radicals



might be attributed to CTC interactions of the radical with the corresponding monomer, resulting in a marked reduction of the free energy of activation for crossed-chain extension.

Several other substituted butadienes, i.e., 2,3-dichlorobutadiene, 1-cyclohexyloxy-1,3-butadiene, 2,3-bis(diethylphosphono)-1,3-butadiene, 2,4-hexadiene, and 1,3-pentadiene, are also claimed to undergo equimolar copolymerization with MA. In addition, the monomer, 1,1-dicyclopentyl-1,3-butadiene is also reported to copolymerize with MA.<sup>(219)</sup> Details on the structure of the copolymers were not available.

Mixtures of 2,4-hexadiene and MA spontaneously copolymerize at 100°C, giving copolymer with m.p. 136–138°C.<sup>(220)</sup> Both bulk and solution copolymerization of the monomer pair, using BPO or AIBN initiators and dioxane solvent, are useful for obtaining alternating copolymerization. In one case, using 1% by weight BPO and dioxane solvent, a copolymer was obtained in 46% yield with m.p. 175–178°C (Table 10.7).

The monomer 2,3-bis(diethylphosphono)-1,3-butadiene also undergoes free-radical-initiated copolymerization with MA.<sup>(221)</sup> In this case, the maximum rate of copolymerization was observed for a 2:1 molar excess of MA.

Heating mixtures of 1-cyclohexyloxy-1,3-butadiene with MA in the presence of methylene blue brings rapid copolymerization.<sup>(222)</sup> For example, heating a benzene solution of the monomers on the steam bath produced in 1 h a 74% yield of equimolar copolymer.

The *cis* and *trans* isomers of piperylene, i.e., *cis*- and *trans*-1,3-pentadienes, differ markedly in their reaction with MA. The *trans*-isomer readily forms a Diels–Alder adduct with MA at 35–70°C (see Chapter 4), while the *cis*-isomer reacts very reluctantly even at 100°C to yield a resinous product accompanied by a small amount of adduct.<sup>(223)</sup> Dioxane and toluene

Table 10.7. Copolymers of Dienes and MA<sup>a</sup>

Diene <sup>b</sup>	Yield (%)	Softening range (°C)	[ $\eta$ ]
Butadiene	9	135–145	—
Isoprene	42	145–152	0.15 <sup>d</sup>
1,3-Pentadiene	41	85–90	0.31 <sup>c</sup>
2,3-Dimethylbutadiene	24	120–125	0.18 <sup>c</sup>
2,4-Hexadiene	46	175–178	0.25 <sup>c</sup>
1-Methoxybutadiene	41	168	0.53 <sup>d</sup>

<sup>a</sup> From Reference 225.

<sup>b</sup> Copolymerizations run in dioxane with 1% (based on monomers) of BPO, AIBN, and *tert*-butyl peroxyvalate.

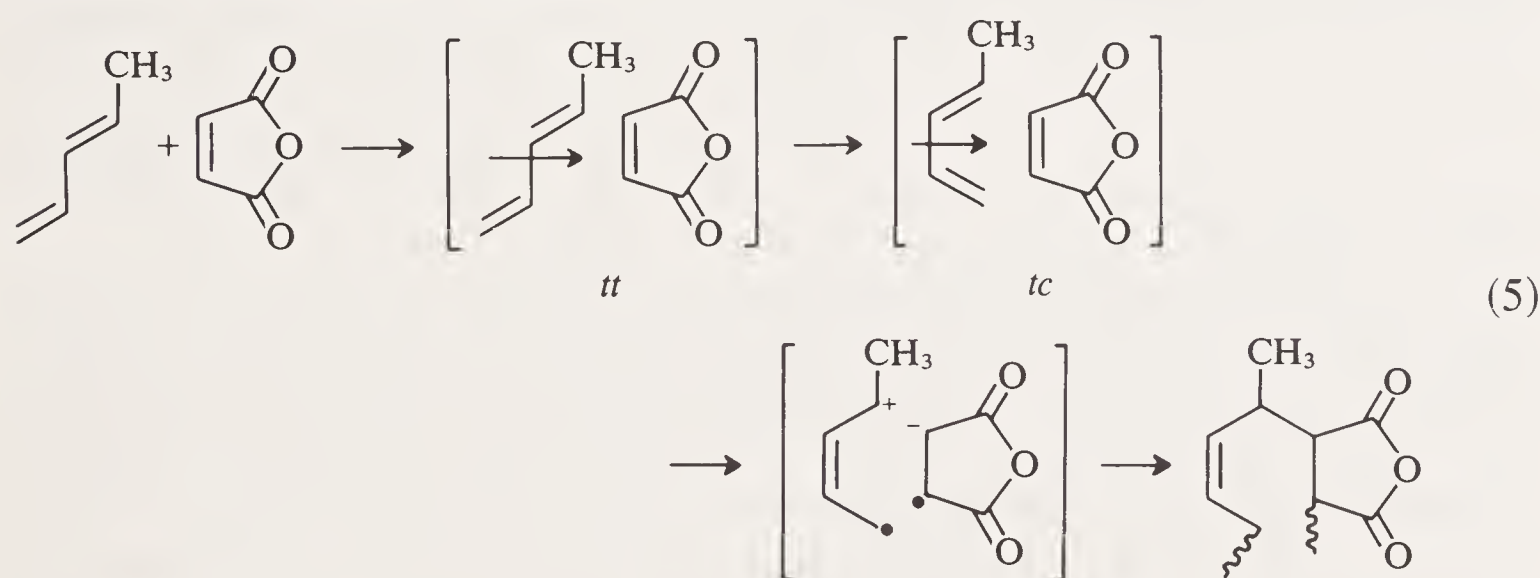
<sup>c</sup> Determined in DMF at 25°C.

<sup>d</sup> Determined in cyclohexanone at 25°C. [ $\eta$ ] values up to 3.2 dl/g also reported.<sup>(225)</sup>

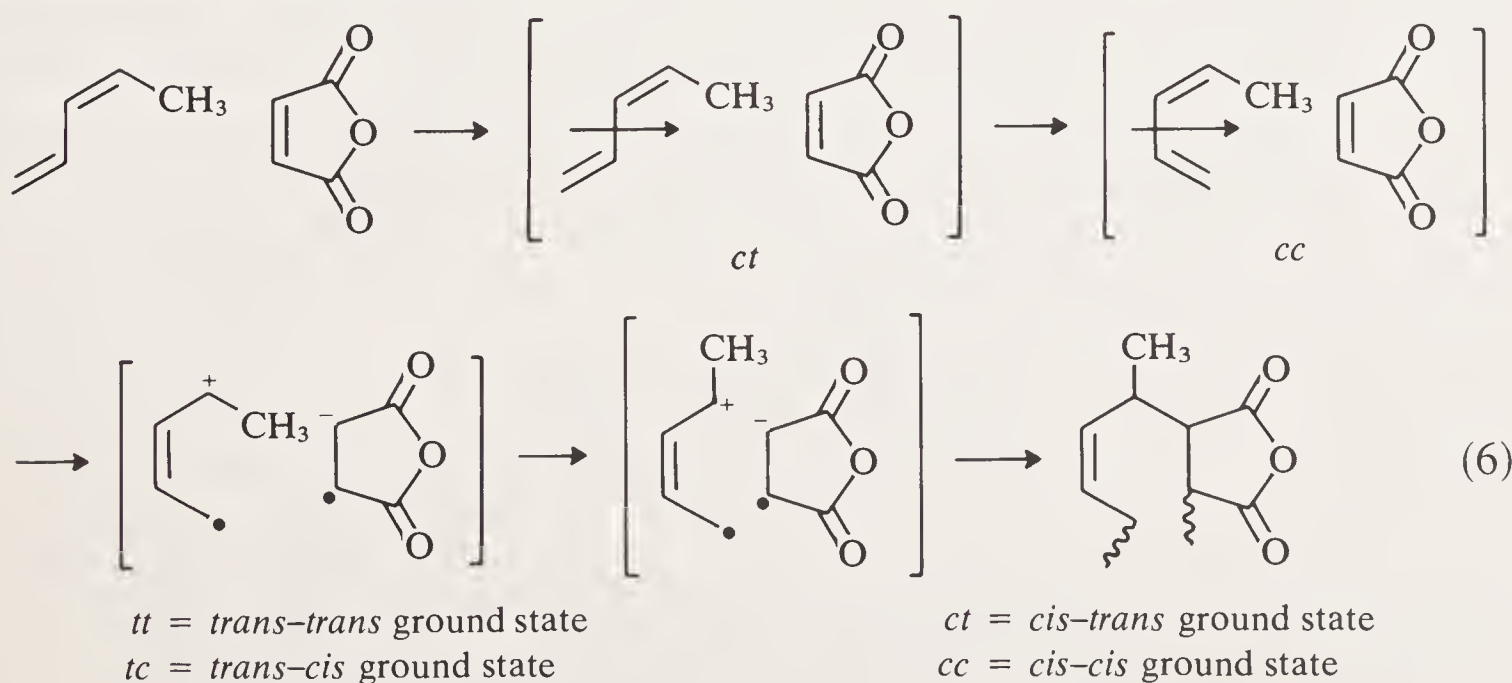


solutions of *cis*-piperylene, *trans*-piperylene, and a mixture of the two isomers were combined with MA and *t*-butyl peroxyphthalate initiator and copolymerized at 70 and 80°C.<sup>(224)</sup> Soluble, equimolar copolymers were obtained in dioxane. The copolymer prepared in toluene from the *trans*-isomer is initially soluble in acetone, but become insoluble rapidly on exposure to air. In contrast, the copolymer of the *cis*-isomer prepared in toluene is insoluble on isolation. The equimolar copolymer was always accompanied by the Diels–Alder adduct in copolymerizations involving the *trans*-isomer or isomer mixture. Yields >80%, with an intrinsic viscosity in 2-butanone (100 ml/g, 25°C) of 0.35 dl/g were obtained for the *cis*-isomer copolymerization in dioxane at 80°C. Yields were somewhat lower for the copolymers prepared from the *trans*-isomer. However, IR and NMR studies showed that identical copolymers were prepared from the two monomers.<sup>(224)</sup>

To account for the above observations, Gaylord and coworkers<sup>(224)</sup> suggest that the alternating copolymerization of *trans*-1,3-pentadiene with MA occurs by the scheme outlined in Eq. (5).



The formation of the same alternating copolymer from the copolymerization of *cis*-1,3-pentadiene with MA is covered in part by the mechanism shown in Eq. (6).<sup>(224)</sup>



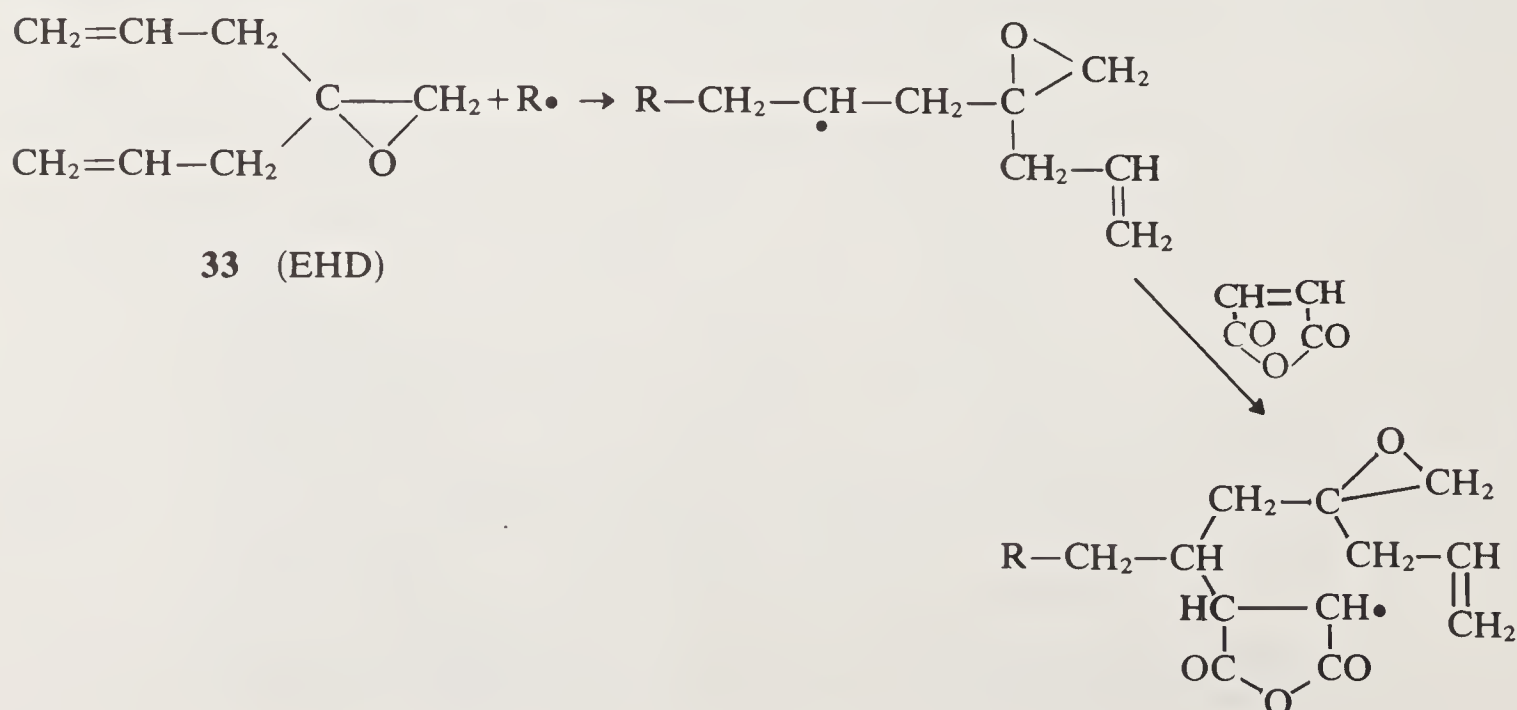
The formation of identical copolymers from both the *cis*- and *trans*-piperylene isomers is thus attributed to the diene–dienophile CTC (see Chapter 4) in an excited state, resulting in the generation of the same homopolymerizable excited-state CTC in both cases.<sup>(224)</sup> The proposed mechanisms do not explain the solubility behavior of the two copolymers.

A comparison of the copolymerization properties of butadiene, isoprene, 2,3-dimethylbutadiene, 2,4-hexadiene, 1,3-pentadiene, and 1-methoxybutadiene with MA is found in Table 10.7. Films obtained by drying solutions of the copolymers were generally tough and flexible. The copolymers contained >75% *cis*-1,4 unsaturation.

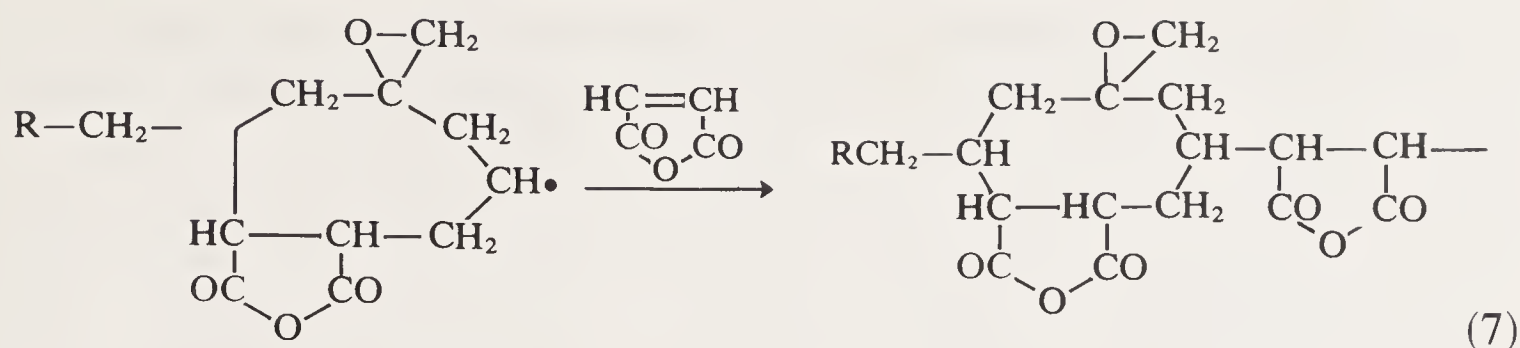
The monomers 1,4-pentadiene,<sup>(125,126)</sup> 1,4-hexadiene,<sup>(227)</sup> and 4,4'-epoxy-1,7-heptadiene<sup>(228)</sup> have had brief study and were shown to undergo cycloliner copolymerization with MA, analogous to that previously reported for the divinyl ether system (Sec. 10.2.4).

Using AIBN initiator, 1,4-pentadiene–MA mixtures were copolymerized in THF for 17–23 h at 50°C. Over the range of monomer feed compositions studied, MA in the copolymers had a mean mole fraction value of 0.67, which is a value predicted for a 2 : 1 (MA : 1,4-pentadiene) molar alternating material. The absence of gelation, even at high conversion and C=C absorption at 6.1  $\mu\text{m}$  in the infrared spectrum gave additional support for the cycloliner alternating structure.<sup>(226)</sup>

Various molar ratios of 4,4'-epoxy-1,7-heptadiene (EHD, **33**) or 2,2-diallyl-oxirane, and MA were copolymerized in 2-butanone for 20 h at 60°C, with 1% by weight BPO. The maximum rate of copolymerization was detected at an EHD : MA feed ratio of 1 : 2. The linearity of the copolymer structure and the independence of the copolymer composition from the starting mixture, i.e., essentially 1 : 2 for various feed ratios, suggests a cycloliner copolymerization mechanism similar to that offered for the copolymerization of diallyl ether (Sec. 10.2.1) and divinyl ether (Sec. 10.2.4) with MA [Eq. (7)].<sup>(228)</sup>





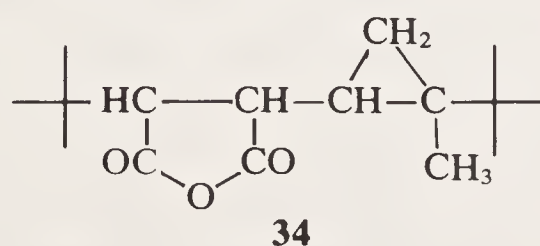


In addition to the main product, small quantities (3–5%) of insoluble product are also formed.<sup>(228)</sup> Additional work is needed to confirm this structure or determine if the copolymer also contains other ring systems. Attempts have also been made to prepare soluble, alternating copolymers of 4-vinylcyclohexene monoxide and MA.<sup>(229)</sup> Even though free-radical copolymerization produced crosslinked materials, it was estimated 1 : 1 copolymerization of the double bonds occurred.

The free-radical copolymerization of 1,3,6-octatriene with MA has received brief study.<sup>(550)</sup> Alternating copolymer containing a 1 : 2 ratio of monomers is claimed.

#### 10.2.12. Cyclic Olefins

A great variety of cyclic olefins, conjugated and unconjugated cyclic dienes, and bicyclic dienes have been copolymerized with MA to give equimolar copolymers. The smallest cyclic olefin 1-methylcyclopropene copolymerizes spontaneously at room temperature with MA, even in bulk or solution.<sup>(230)</sup> The electron availability in the cyclopropene double bond promotes ready copolymerization of the monomer with electron-acceptor monomers such as MA and sulfur dioxide, even in the absence of initiator. Ether solvents, such as THF and dimethoxyethane, work best, eliminating side reactions or nonpolymeric product. Typically, a 70% conversion is reached in 18 h in ether solution and the copolymer has an intrinsic viscosity, measured in acetone at 25°C, of 0.80 dl/g. This is a much higher intrinsic viscosity than normally obtained for MA–cycloolefin copolymerizations. Composition, IR, NMR, and solubility characteristics indicate the copolymer has a 1 : 1 alternating structure **34**. Dialkyl fumarates also copolymerize well with 1-methylcyclopropene to give equimolar copolymer.



A film of the copolymer **34**, which is readily soluble in polar solvents, has a rigid glass character and softens near 300°C. Differential thermal and



Table 10.8. Copolymerization of Cyclic Olefins ( $M_1$ ) with MA ( $M_2$ )<sup>a</sup>

$M_1^b$	Time (h)	Yield (%/h)	Softening point (°C)	$\bar{M}_w^c$
Cyclobutene	0.32	41.8	180–190	Insoluble
Cyclopentene	1.25	21.0	190–195	1 600
Cyclohexene	23.00	0.8	170–185	500
Cycloheptene	19.00	1.0	240–245	700
Cyclooctene	14.00	1.4	250–255	1 600

<sup>a</sup> From Reference 232.  
<sup>b</sup> Copolymerizations run in benzene at 60°C with MA = [olefin] = 1.54 mole/liter and [AIBN] =  $3.2 \times 10^{-2}$  mole/liter.  
<sup>c</sup> Vapor pressure osmometer values.

thermogravimetric analysis indicate the polymer starts to decompose at approximately 300°C. The low hydrogen content and the general resistance of cyclopropane hydrogens to abstraction by free radicals contribute to stabilizing the copolymer to discoloration on prolonged heating at 150°C.<sup>(231)</sup>

Cyclobutene,<sup>(232)</sup> cyclopentene,<sup>(232–237)</sup> methylenecyclopentene,<sup>(238)</sup> cyclohexene,<sup>(234,235)</sup> cycloheptene,<sup>(232)</sup> cyclooctene,<sup>(232)</sup> bicyclo[2.2.1]hepta-2-ene (norbornene),<sup>(239–241)</sup> and some derivatives of norbornene<sup>(242)</sup> are also known to copolymerize with MA to give noncrystalline equimolar copolymers.

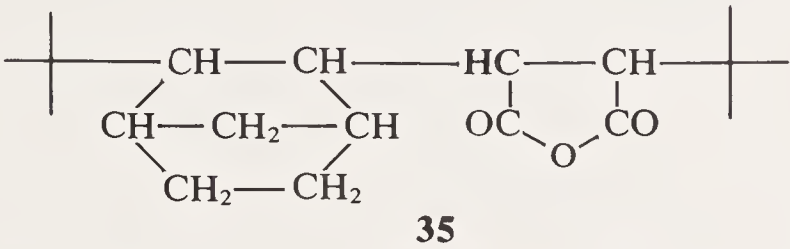
Copolymerizing equimolar amounts of C<sub>4</sub>–C<sub>8</sub> cyclic olefin with MA gives the results shown in Table 10.8. Changing the copolymerization temperature in Table 10.8 to 80°C and using BPO produced both higher yields and higher molecular weights, with reduced cycle time, for the cyclopentene–MA and cyclohexene–MA monomer pairs.<sup>(234)</sup> For example, running polymerization of both pairs for 10 h produced cyclopentene– and cyclohexene–MA copolymers having molecular weights, respectively, of 6 400 and 2 600.

Considering cyclopentene as representative of the cyclic olefins, the kinetics of its copolymerization with MA was investigated.<sup>(232)</sup> The copolymerization rate data showed a maximum rate at approximately 40 mol % MA. An Arrhenius plot of the rate data and interpretation of the results yielded an overall activation energy of  $24.2 \pm 0.35$  kcal/mol. No thermal initiation was detected for the C<sub>4</sub>–C<sub>8</sub> olefin–MA copolymerizations.<sup>(235,236)</sup>

Free-radical copolymerization of cyclopentene with MA has also been studied at pressures up to 6 000 kg/cm<sup>3</sup>.<sup>(237)</sup> At 60°C, the rate of copolymerization increased with pressure and the conversion at 6 000 kg/cm<sup>3</sup> attained a maximum constant value in a short time. For a given monomer feed, the content of cyclopentene in the copolymer increased with pressure. A maximum rate of copolymerization was observed at about 0.6 mol fraction cyclopentene. No pressure dependence of the molecular weight was noted for the copolymers

and the molecular weights were approximately 2 900. The rate of copolymerization of cyclohexene with MA is also enhanced with pressure.<sup>(187)</sup>

From early studies on the copolymerization of bicyclo[2.2.1]hept-2-ene (norbornene) with MA, it was concluded that mixtures of these two monomers would suffer spontaneous polymerization.<sup>(239)</sup> For example, heating mixtures of the two monomers for several hours in cyclohexanone at 90°C gave good yields of alternating copolymer **35**, having a reduced viscosity of 0.11 dl/g (cyclohexanone, 30°C).



Others repeated the above work and arrived at a different conclusion.<sup>(240–243)</sup> Only traces of copolymer are obtained when freshly distilled norbornene and cyclohexanone are used and oxygen is excluded, indicating hydroperoxide must account for the earlier spontaneous polymerization results.<sup>(241,243)</sup> Although norbornene–MA copolymers have equimolar composition, the polymerization rate is claimed to be maximum at an anhydride–norbornene ratio of 2 : 1.<sup>(241)</sup> This suggests the possible presence of a highly reactive 2 : 1 CTC, even though propagation appears to occur by a 1 : 1 mechanism. The copolymerization rate has been shown to be enhanced as pressures are raised from 1 bar to 3 kbars, with the alternating structure retained.<sup>(187)</sup> The above picture is made more cloudy by additional copolymerization results (Table 10.9), which suggests the maximum rate for the norbornene–MA pair occurs at equimolar mixtures.

Several different substituted norbornenes **36** have also been copolymerized with MA, using AIBN initiator.<sup>(244,245,274)</sup> However, only the *exo*- and *endo*- isomers of 5-cyanobicyclo[2.2.1]hept-2-ene **36D** is claimed to undergo equimolar copolymerization with MA.

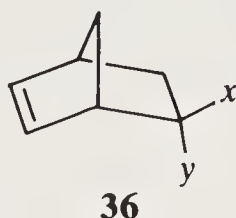
Table 10.9. Copolymerization of Norbornene with MA<sup>a</sup>

Norbornene (mmole)	MA (mmole)	Time (h)	Conversion (%)	Norbornene in copolymer (mol %)	[η] (dl/g)
20	60	20	27.1	50	0.15 <sup>c</sup>
40	40	20	36.5	50	0.21
60	20	20	27.6	50	0.14

<sup>a</sup> From Reference 240. Copolymerizations run in toluene at 60°C, with 0.8 mmole AIBN.  
<sup>b</sup> [η] Values determined in dimethylsulfoxide at 30°C.



The above is surprising, since the large negative  $e$  value for norbornene monomers **36A–36C** (Table 10.10) suggests that these monomers, rather than **36D**, should have the greatest preference to undergo alternating copolymerization with MA, which has a large positive  $e$  value.



- A**  $X = \text{H}, Y = \text{CO}_2\text{CH}_3$   
**B**  $X = \text{CH}_3, Y = \text{CO}_2\text{CH}_3$   
**C**  $X = \text{H}, Y = \text{COCH}_3$   
**D**  $X = \text{H}, Y = \text{CN}$

For both the *exo*- and *endo*-isomers of **36D**, the maximum rates of copolymerization occur at 1:1 monomer mixtures.<sup>(244)</sup> Specific viscosities of the resulting materials were quite low and did not change with the composition of the initial monomer mixture.

There is some indication that norbornenecarboxylic acid will also undergo equimolar copolymerization with MA, using both free-radical and radiation ( $^{60}\text{Co}$ ) initiation.<sup>(274)</sup> Some decarboxylation, attributed to the norbornenecarboxylic acid, occurs during both polymerizations. The composition of the copolymers is independent of the method of initiation and of the initial comonomer feeds. However, Nyitray and Hardy<sup>(242)</sup> claim significant self-addition of MA may occur from copolymerization of eutectic mixtures of norbornenecarboxylic acid–MA.

Bailey<sup>(532)</sup> recently reported that  $\beta$ -pinene will undergo equimolar copolymerization with MA, in the presence of peroxide initiators, to give unique polymers **37**. In the absence of peroxides, the two compounds will only undergo thermal addition to give an “ene” product (see Chapter 6).<sup>(533)</sup> The copolymerization mechanism is believed to be as follows [Eq. (8)]:

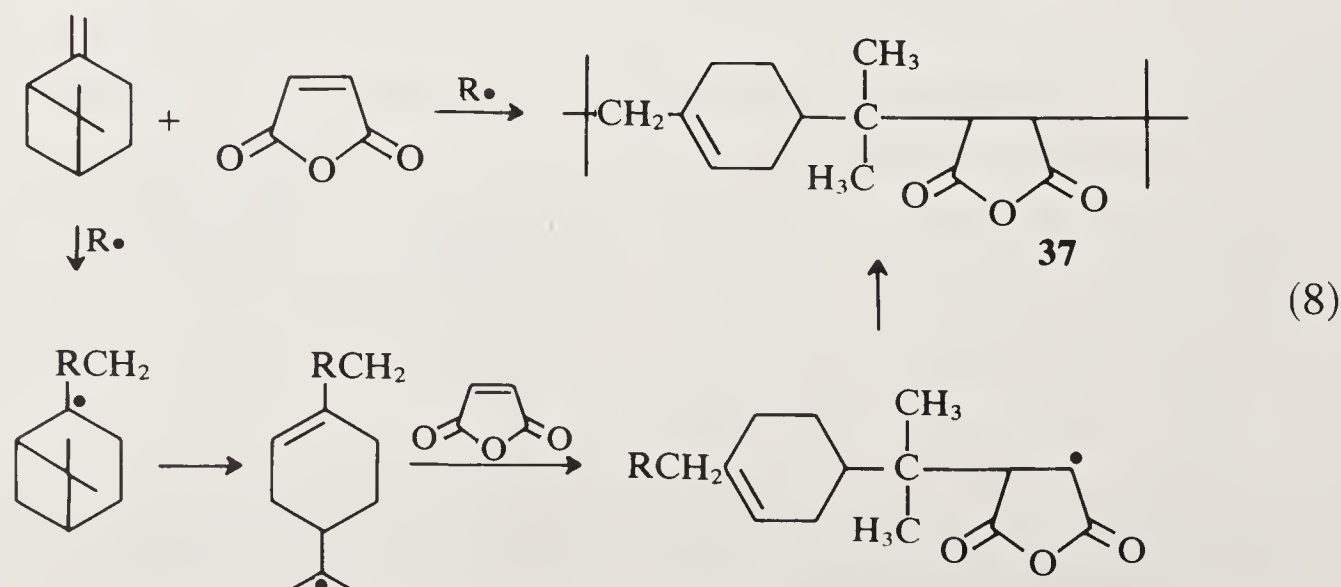




Table 10.10. *Q* and *e* Values for Norbornene Monomers **36**<sup>a</sup>

Monomer	<i>Q</i>	<i>e</i>
A	0.31	−2.29
B	0.31	−2.29
C	0.064	−2.45
D	0.016	0.58
MA	0.230	2.25
Norbornene	0.09	−1.04

<sup>a</sup> From References 41, 244, and 272.

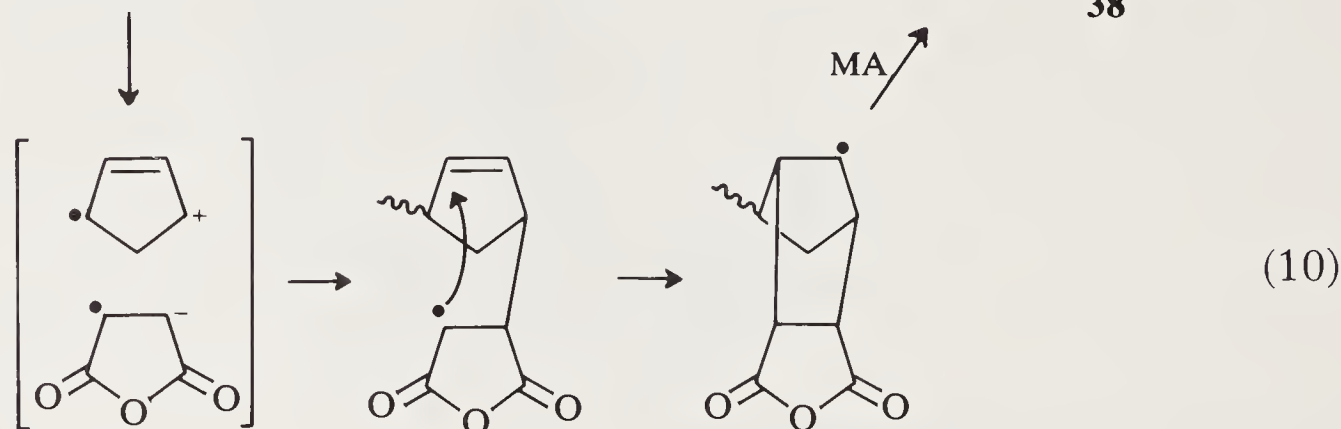
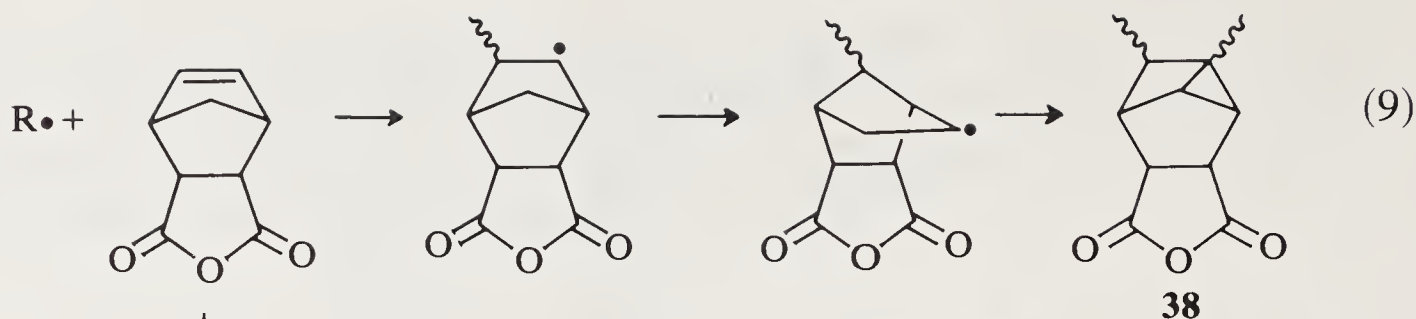
10.2.13. Cyclodiene Monomers

Several conjugated and nonconjugated cyclodienes, such as cyclopentadiene,<sup>(246–249)</sup> 1,4-cyclohexadiene,<sup>(250)</sup> 1,3-cycloheptadiene,<sup>(251,252)</sup> 1,3-cyclooctadiene,<sup>(251,252)</sup> and 1,5-cyclooctadiene,<sup>(32,253)</sup> 3-(4'-pentenyl)-cyclopentene-1,<sup>(254)</sup> 3-allylcyclopentene, 4-allylcyclopentene, 3-allylcyclohexene, and 4-allylcyclohexene,<sup>(255)</sup> exhibit capability to undergo either a 1 : 2 or 1 : 1 alternating copolymerization with MA.

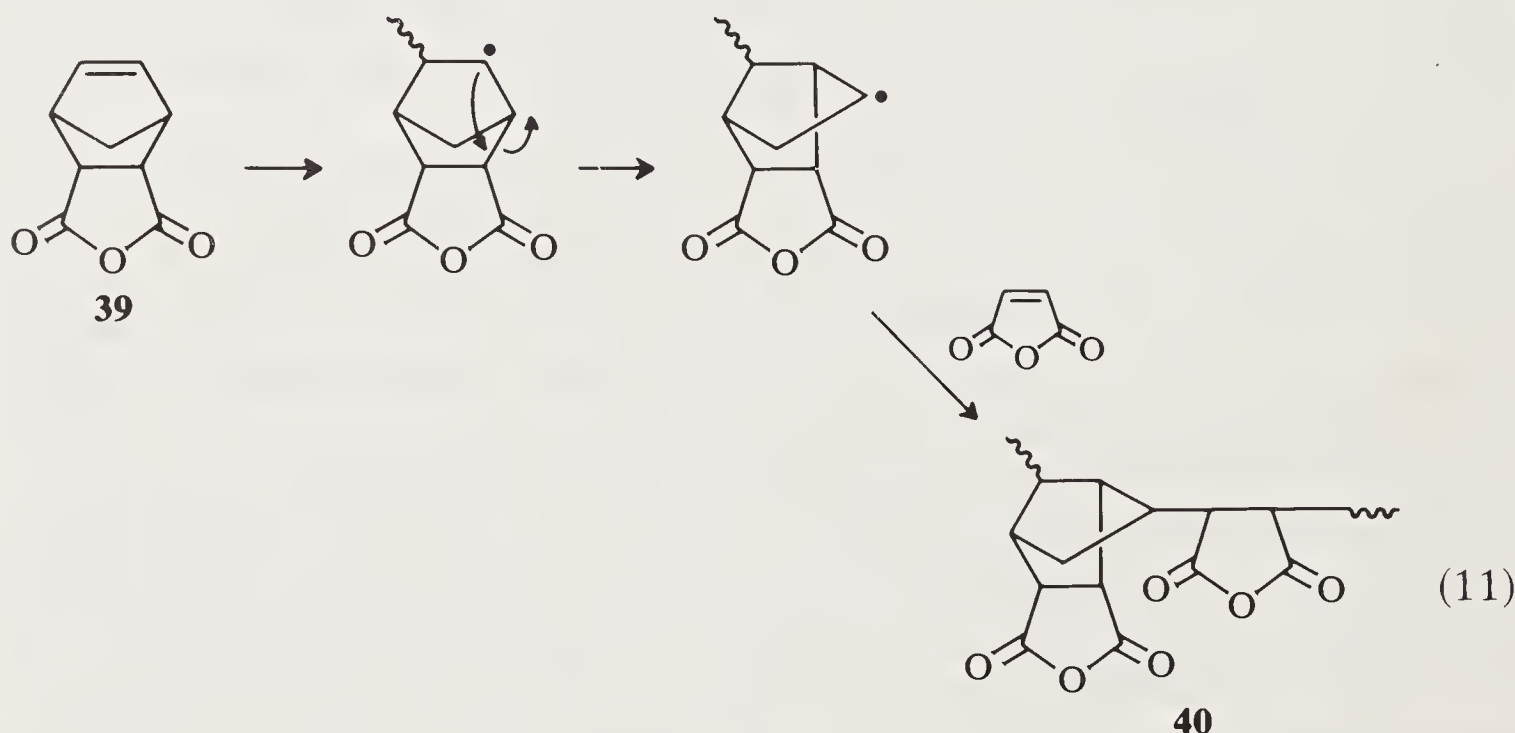
In the absence of radical initiators, cyclopentadiene and MA form a 1 : 1 Diels–Alder adduct, bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic anhydride (see Chapter 4). The *endo*-adduct formed below 170°C, undergoes isomerization above 170°C to the *exo*-adduct.<sup>(256)</sup> Both the *endo*- and *exo*-adducts undergo homopolymerization to yield polymer containing equimolar amounts of the two monomers.<sup>(249)</sup> Copolymerization occurs in the presence of radical initiators at a temperature where the initiator has a short half-life. For example, heating molten *endo*-adduct with 6.6 mol % *tert*-butylhydroperoxide for 1 h at 240°C gives 83% copolymer. Heating the *exo*-adduct with 10 mol % *t*-butyl peracetate in chlorobenzene for 1 h gives a 72% yield of copolymer.

When copolymerizations are conducted below the *endo*–*exo* isomerization temperature, e.g., 80–155°C, the low-molecular-weight (<3 000) polymer retains the starting monomer configuration **38**. Above 200°C, the polymer contains both configurations; i.e., isomerization occurs. Gaylord and co-workers<sup>(246–248)</sup> believe the reaction run at lower temperature proceeds as illustrated in Eq. (9); whereas, at higher temperature the mechanism probably includes a CTC intermediate generated by retrograde dissociation, Eq. (10). Gaylord and Martan<sup>(1118)</sup> have recently proposed that isomeric *N*-phenyl-5-norbornene-2,3-dicarboximides experience a similar polymerization profile.

The 1 : 1 cyclopentadiene–MA adduct, in the presence of peroxide initiators undergoing rapid thermal decomposition, will also copolymerize to yield 1 : 1 alternating copolymers in which cyclopentadiene and MA are

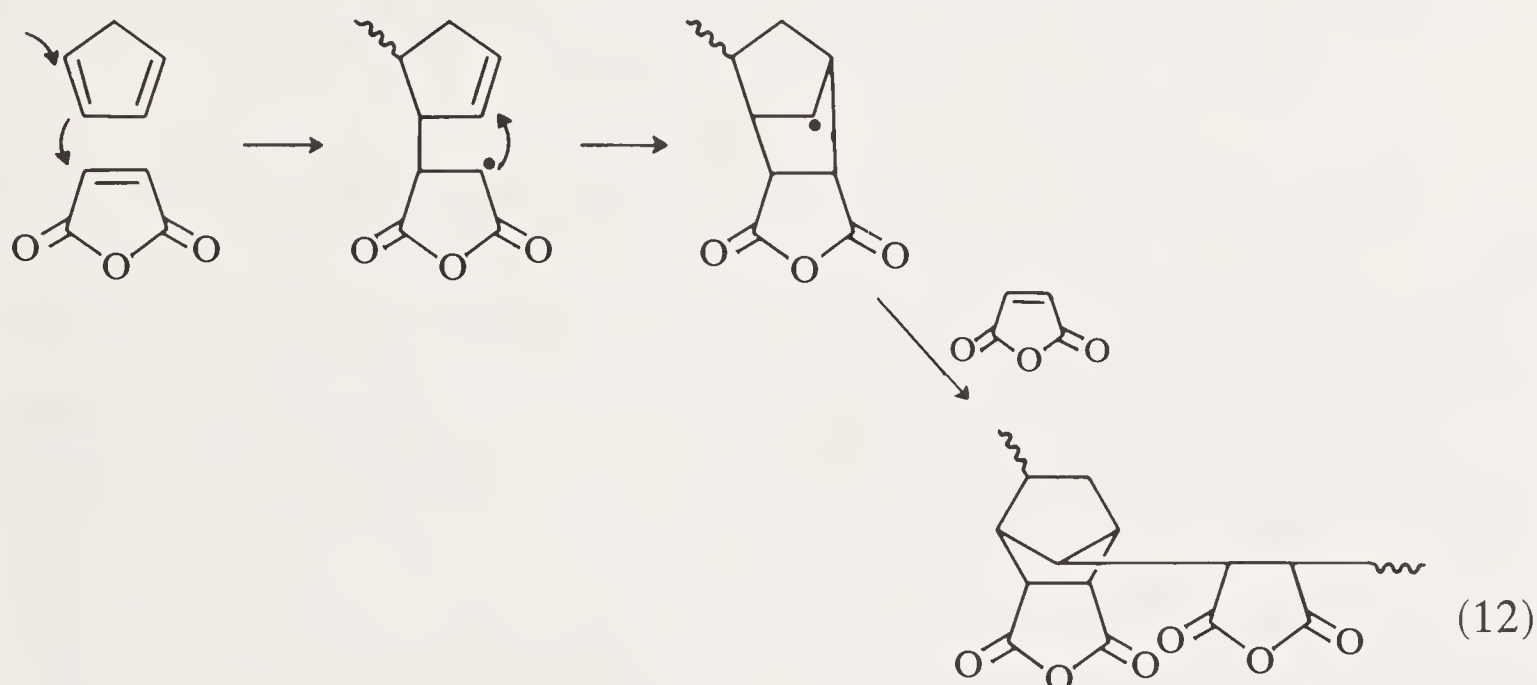


present in 1:2 molar ratio.<sup>(248)</sup> Heating an equimolar mixture of **39** and MA at 155°C and subsequently adding 5 mol % *tert*-butyl peracetate over 20 min in several portions produced a 71% yield of copolymer **40**. The suggested route to copolymer **40** is shown in Eq. (11).<sup>(248)</sup>

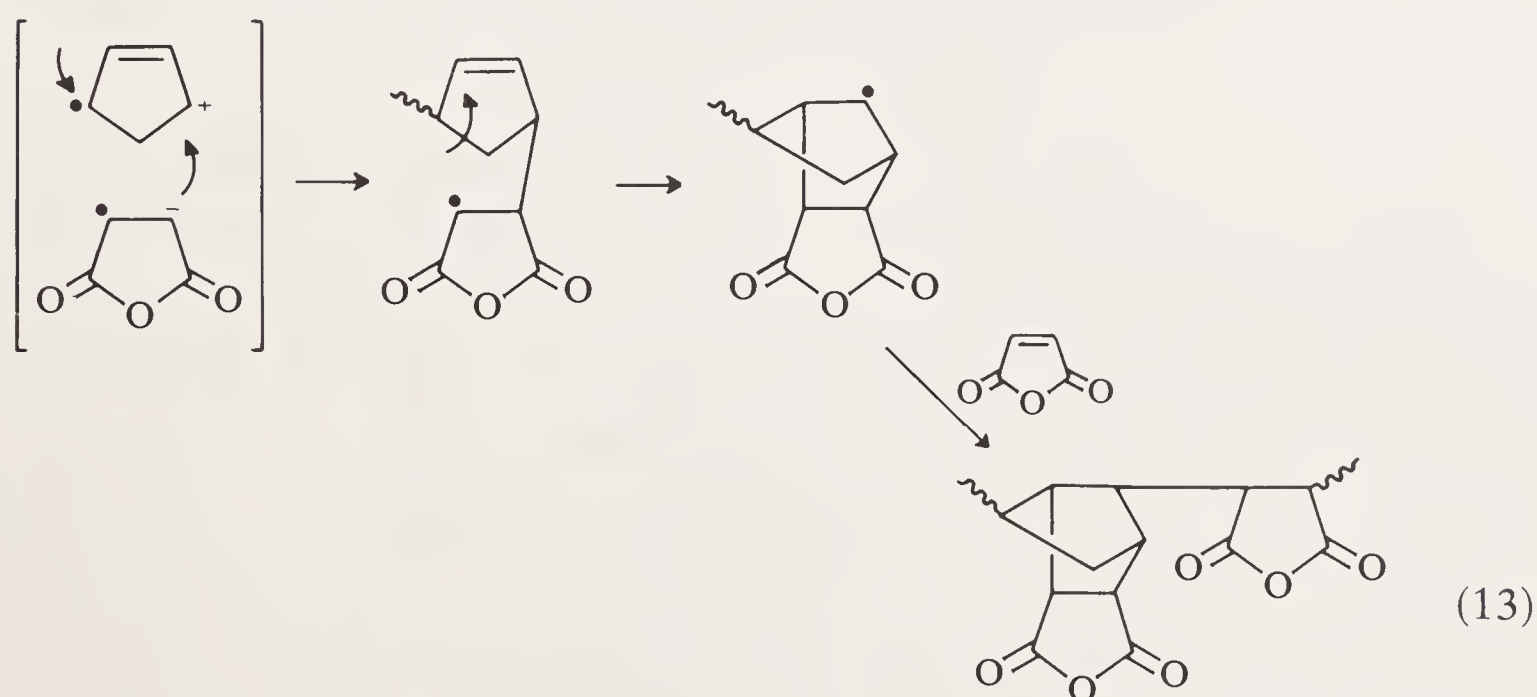


Under appropriate conditions and in the presence of free-radical initiators, cyclopentadiene and MA will also react to form a saturated 1:2 copolymer.<sup>(249)</sup> Copolymerizations are most effectively carried out at 80–205°C. In general, the highest yield of 1:2 copolymer is obtained when the initiator is used at a temperature where it has a short half-life. At a given temperature, the higher the initiator concentration or more rapidly the initiator decomposes, the higher the yield, independent of total reaction time. Copolymerizations may be run in bulk or solvents such as dioxane or chlorobenzene. The amount of solvent is critical, i.e., the yield of copolymer decreases with increasing solvent concentration unless the initiator concentration is increased.

The 1:2 cyclopentadiene-MA copolymer composition, with molecular weight 500–1 000 and softening point 260–280°C, is dependent on the initial monomer charge and the reaction temperature.<sup>(248)</sup> For example, heating an equimolar mixture of the two monomers at 155°C for 20 min with 2 mol % *tert*-butyl peracetate gives 57% copolymer. Composition, IR, and NMR studies suggest a mechanism wherein a 1:1 CTC undergoes cyclopolymerization with MA,<sup>(249)</sup> Eq. (12).



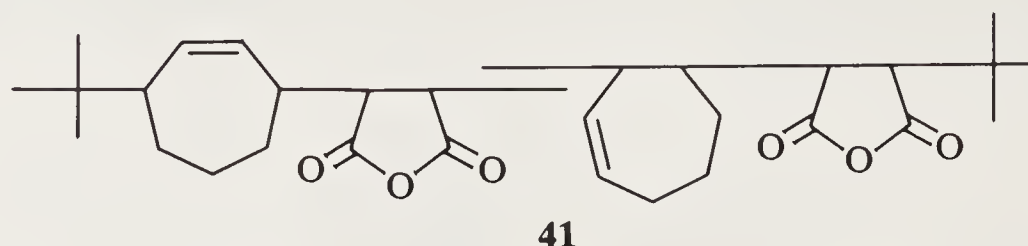
The reaction conditions needed to promote cyclopentadiene-MA copolymerization, i.e., rapid initiator concentration, prompted Gaylord *et al.*<sup>(248,249,258)</sup> to suggest that copolymerization proceeds through reaction of an excited CTC (exciplex), as shown in Eq. (13). Additional studies are needed to substantiate the speculative rearrangement mechanisms advanced in Eqs. 9–13.



The monomer 1,3-cycloheptadiene, with conjugated double bonds, forms a light yellowish-green colored solution when combined with MA. Upon



heating for 5 h at 6°C, a low yield (16.5%) of copolymer may be separated from the Diels–Alder adduct (see Chapter 4).<sup>(251,252)</sup> The copolymer, with observed C = 68.30% and H = 6.51% (theory for 1:1 copolymer: C = 68.53%, H = 6.25%) and softening point 205–215°C, is believed to have structure **41**.



Adding AIBN initiator to the mixture greatly improves the yield, i.e., after 3 h at 60°C a 65.2% of **41** was obtained, having a specific viscosity in 2-butanone of 0.15 dl/g (0.5 g/100 ml, 25°C). Infrared and NMR spectra of both copolymers were consistent with **41**.

Not much variation in yield of the 1:2 cycloheptadiene–MA Diels–Alder adduct is noticed even after addition of initiator. The yield reached a maximum at a 1:1 ratio of monomers, consistent with a suggestion that both the polymerization and adduct reaction proceed via a CTC having a 1:1 ratio of the monomer pair.<sup>(251,252)</sup> A large decrease in reaction rate occurs upon the addition of small amounts of several solvents. Concluding that the concentration of both reaction products can possibly be represented by the concentration of charge-transfer complexes for the reactions and that the reaction rate constant is highest for the copolymerization, a suggestion is made that initiating radicals for the copolymerization are produced from a CTC formed between the monomer pair.

Maleic anhydride and 1,3-cyclooctadiene will not undergo a Diels–Alder reaction. Also, in contrast to 1,3-cycloheptadiene, 1,3-cyclooctadiene requires

Table 10.11. Copolymerization of 1,3-Cyclooctadiene with MA<sup>a</sup>

Initiator <sup>b</sup>	Solvent	Conditions <sup>c</sup>	Conversion (%)	$\eta$ sp/C (dl/g)
AIBN	Acetic anhydride	Homogeneous	34.5	0.21 <sup>d</sup>
BPO	Acetic anhydride	Homogeneous	24.4	0.21
AIBN	Benzene	Heterogeneous	28.7	0.23
BPO	Benzene	Heterogeneous	21.2	0.23
AIBN	Acetone	Homogeneous	19.7	0.19
AIBN	Dimethyl formamide	Homogeneous	0	—
AIBN	1,4-Dioxane	Homogeneous	19.1	0.21

<sup>a</sup> From Reference 259.

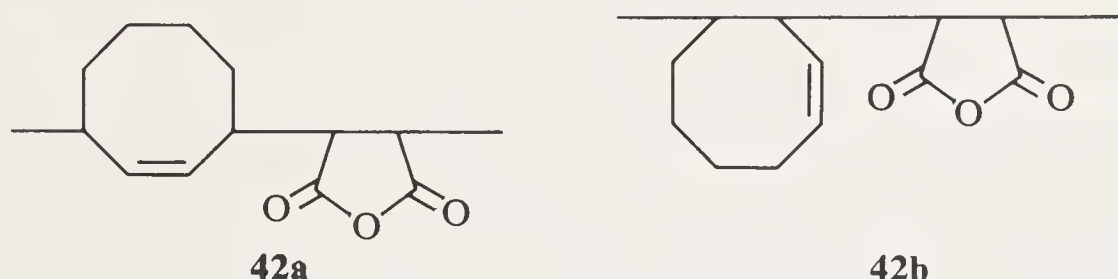
<sup>b</sup> [AIBN] = [BPO] =  $2 \times 10^{-2}$  mole/liter.

<sup>c</sup> [1,3-Cyclooctadiene] + [MA] = 1.0 mole/liter; temperature, 50°C; time, 24 h.

<sup>d</sup> Specific viscosities determined in DMF (0.5 g/100 ml, 25°C).

an initiator to copolymerize with MA.<sup>(251,259)</sup> Table 10.11 shows the results of several copolymerizations of equimolar amounts of 1,3-cyclooctadiene with MA.

The 1,3-cyclooctadiene-MA copolymers are white powders, soluble in acetone, 2-butanone, acetic anhydride, DMF, and dioxane, with a melting point near 210°C.<sup>(251,259)</sup> Elemental, IR, and NMR results are consistent with structures **42a** and **42b**.



The MA content of the copolymer did not depend on the monomer concentrations and was always near 50 mol %, meaning the 1,3-cyclooctadiene-MA ratio of the copolymer was near 1 : 1. On the other hand, specific viscosities and yield of copolymer reached a maximum at equimolar starting mixtures.

Using AIBN, the total activation energy was calculated to be 22.7 kcal/mol and the copolymerization rate (propagation rate) obeyed the following equation.

$$R_p = k[\text{AIBN}]^{0.8}[\text{M}]^{1.3}$$

$$[\text{M}] = [1,3\text{-Cyclooctadiene}] + [\text{MA}]$$

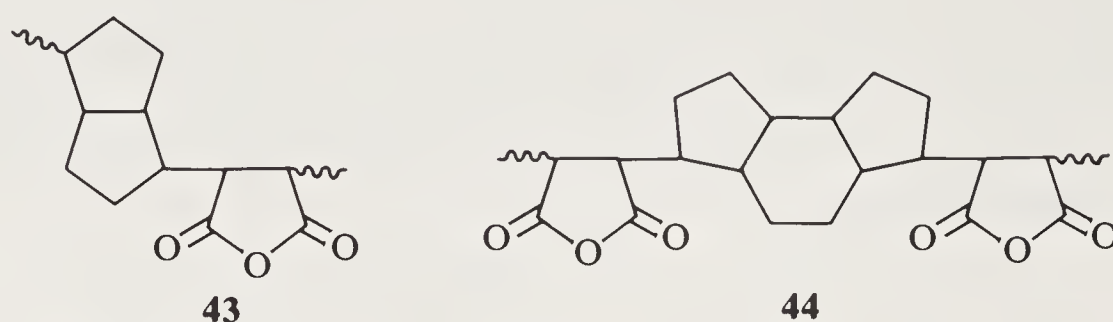
where:  $[1,3\text{-cyclooctadiene}] = [\text{MA}]$  and for BPO

$$R_p \propto [\text{BPO}]^{0.7}$$

The monomer *cis*, *cis*-1, 5-cyclooctadiene, in contrast to 1,3-cyclooctadiene, thermally copolymerize with MA.<sup>(32,253)</sup> Heating a 1:2 (MA:1,5-cyclooctadiene) mixture for 20 h at 150°C produces essentially a 100% yield of white amorphous polymer, m.p. 150°C. Copolymerization may also be run in a variety of solvents, although low boiling solvents require the addition of free-radical initiators. Xylene appears to be best, giving a copolymer with m.p. 200°C. The ratio of the monomer pair in starting mixture does not appear to unduly influence the composition of the copolymer, the latter being close to 1:1. The molecular weight of the butyl ester was determined by vapor pressure osmometry as 3 550, corresponding to about 116 monomer pair repeating units.

The copolymer is not strictly alternating, since MA seems only to be incorporated in the intermolecular step; the intramolecular step being a transannular reaction of the cyclooctadiene. On the basis of composition, IR and NMR studies, and failure of the polymer to take up bromine, a

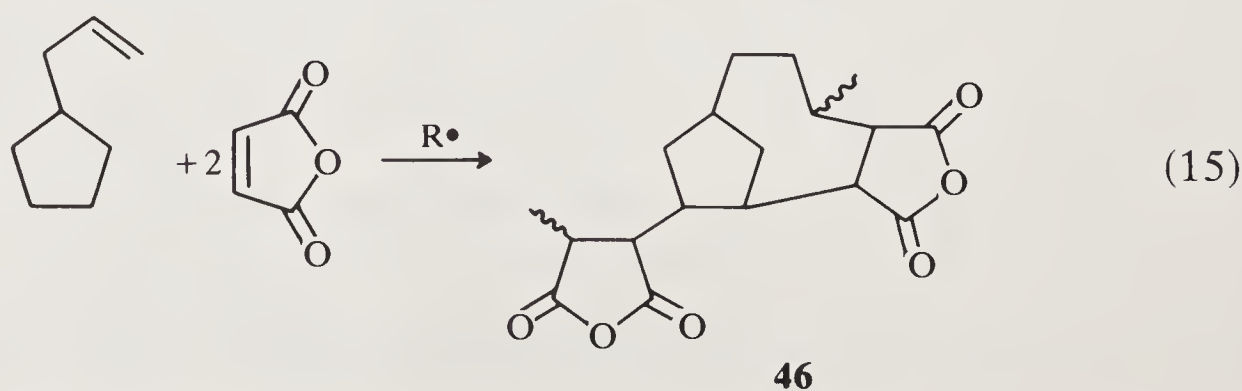
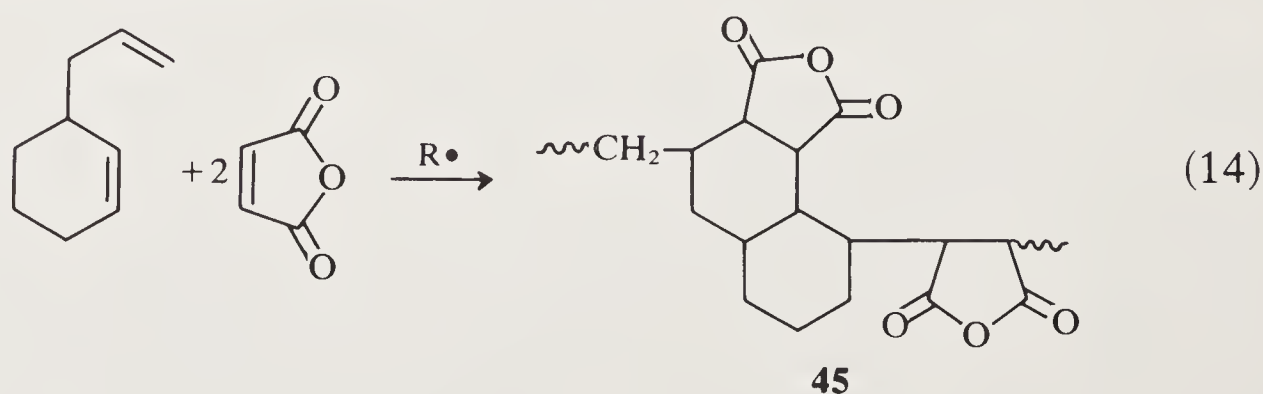
transannular cyclocopolymerization mechanism is proposed to account for the 1:1 copolymer **43**.



Maleic anhydride copolymerization with *cis*, *trans*, *trans*-, and *trans*, *trans*, *trans*-cyclododecatriene have also been explored.<sup>(535)</sup> Copolymerization in dioxane, with AIBN, gave white powders showing softening points  $>300^{\circ}\text{C}$ . The copolymer was soluble in polar solvents and exhibited an NMR spectrum supportive of structure **44**.

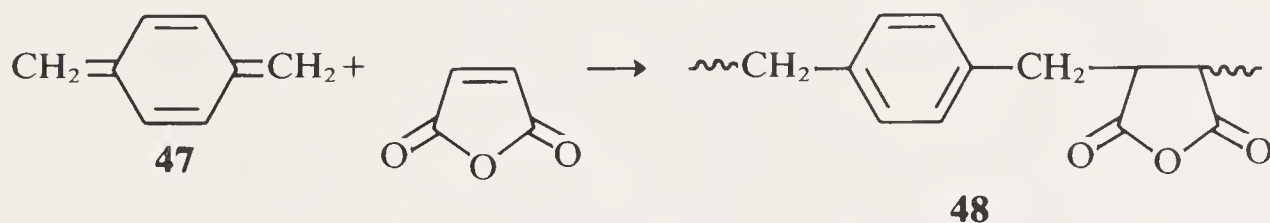
The monomers 4-vinylcyclohexene and 1,5,9-cyclododecantriene have also been copolymerized with MA.<sup>(32,255)</sup> Copolymerization in both cases were run in benzene at  $60^{\circ}\text{C}$  with AIBN, using various molar ratios of the two different monomer pairs. In the case of 4-vinylcyclohexene, the low-molecular-weight copolymers for each run was essentially a 2:3 molar composition of vinyl-cyclohexene to MA. Copolymerization of 1,5,9-cyclododecatriene with MA produced insoluble material. Copolymer composition studies showed these materials tended to be alternating.

The monomers 3-allylcyclopentene and 3-allylcyclohexene produce soluble copolymers with MA.<sup>(255)</sup> Copolymer composition studies show the materials to be 2:1 molar in MA and diene residues **45** and **46**. As shown, a cyclic copolymerization mechanism is also advanced for the formation of the multicyclic repeating units [Eqs. (14) and (15)].





While studying the chemistry of *p*-xylylene **47**, Errede and Hoyt<sup>(260)</sup> discovered the monomer would readily undergo equimolar copolymerization with MA, fumarates, and maleates. A *p*-xylylene-toluene solution was added slowly to a toluene-MA mixture, at  $-78^{\circ}\text{C}$ , to produce 1:1 copolymer **48**.



#### 10.2.14. Bicyclodiene Monomers

A variety of nonconjugated bicyclodienes, where the olefin residues are part of two fused rings, such as dicyclopentadiene, or part of two separate but connected rings, such as 1,1'-bicyclopent-2,2'-ene, have been investigated in copolymerization studies with MA.

The cyclocopolymerization of MA with the four bicyclic dienes 1,1'-bicyclopent-2,2'-ene **49**, 1,1'-dicyclohex-2,2'-ene **50**, 1,1'-dicyclopent-2,2'-enyl ether **51**, and 1,1'-dicyclohex-2,2'-enyl ether **52** leads to soluble, low-molecular-weight polymers approaching a 2:1 comonomer ratio,<sup>(261)</sup> Table 10.12.

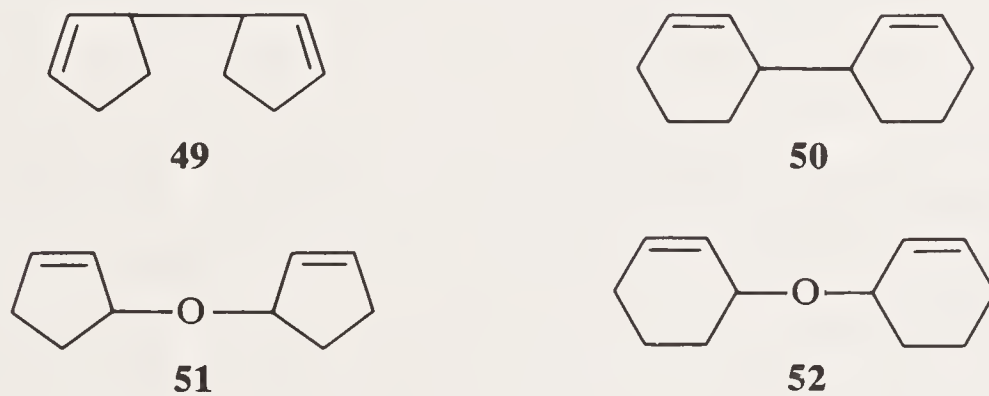


Table 10.12. Copolymerization of BCP, BCH, DCPE, and DCHE (**49–52**) with MA<sup>a,b</sup>

Diene (mole $\times 10^{-3}$ )	MA (mole $\times 10^{-3}$ )	Conversion <sup>c</sup> (mol %)	$[\eta]^d$ (dl/g)	Softening point ( $^{\circ}\text{C}$ ) <sup>e</sup>
BCP (3.6)	7.6	45.4	0.037	200
BCH (3.0)	12.0	28.3	0.033	194
DCPE (3.0)	12.0	54.4	0.039	218
DCHE (3.0)	12.0	21.0	0.029	198

<sup>a</sup> After Reference 261. By permission of John Wiley & Sons, Inc., New York, New York.

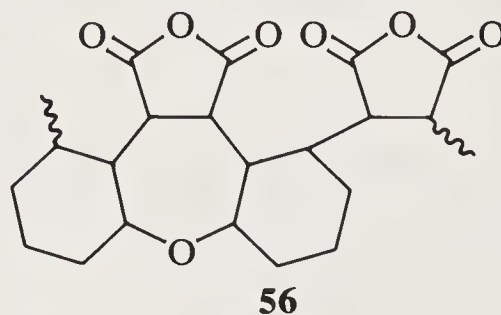
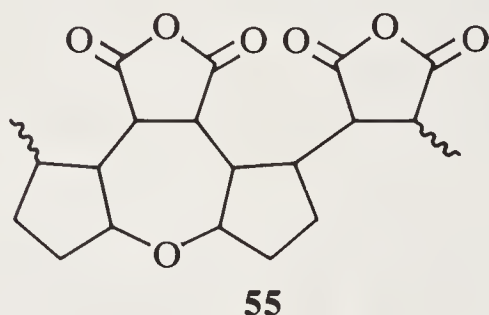
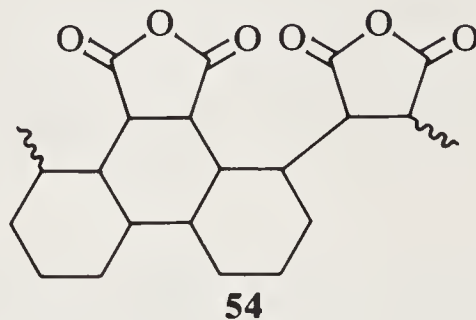
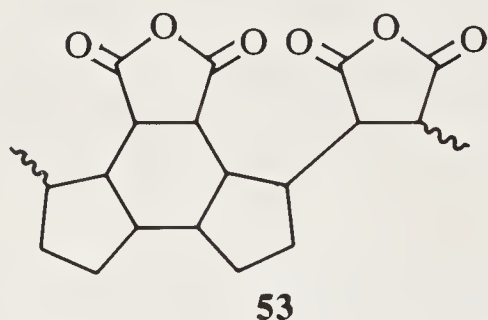
<sup>b</sup> Copolymerizations run for 40 h in acetic anhydride at  $70^{\circ}\text{C}$ , with 5 wt. % AIBN.

<sup>c</sup> Based on diene.

<sup>d</sup> Intrinsic viscosities determined in THF (0.5 g/100 ml) at  $25^{\circ}\text{C}$ .

<sup>e</sup> Determined in air on a Kofler hot bench.

Since the resulting copolymer compositions did not deviate appreciably from the proposed fused structures **53**–**56**, additional studies were mostly confined to BCP, where a slight excess of MA was sufficient to obtain conversions of 40–60%.

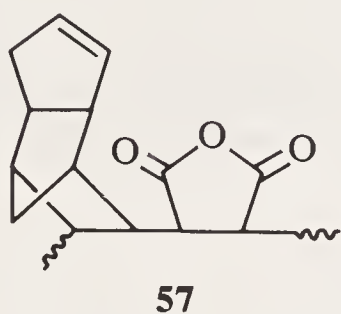
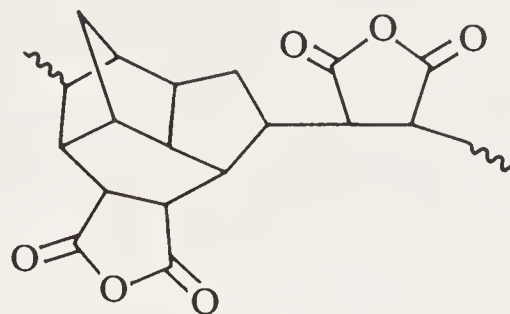


Both peroxides and azodinitrile initiators were found to be effective. However, *p*-chlorobenzoyl peroxide gave the highest conversions.<sup>(258)</sup> Compared to benzene, acetic anhydride was the preferred polymerization medium, since this solvent maintained homogeneous conditions and gave best yields. Akin to the results reported earlier<sup>(262)</sup> for the homopolymerization of MA (see Chapter 8), the combination of acetic anhydride and AIBN was most effective. Polymer composition **53** was independent of the conversion, as expected for an alternating system. Conversion strongly depended on initiator concentration, however, the inherent viscosity appeared to be completely independent of the initiator concentration. The copolymers **53**–**56** are colorless powders, soluble in a variety of organic solvents.

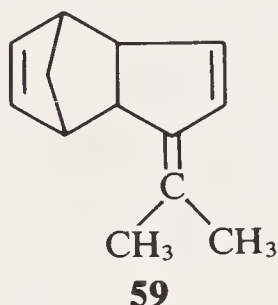
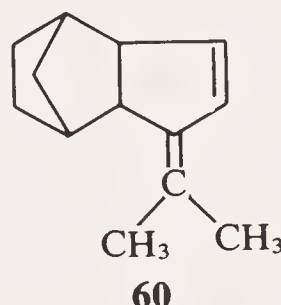
Dicyclopentadiene is claimed to readily undergo equimolar cyclocopolymerization with MA, with free-radical initiators at temperatures below 170°C.<sup>(263)</sup> Above 170°C, dissociation of dicyclopentadiene occurs, giving terpolymers of cyclopentadiene, dicyclopentadiene, and MA.<sup>(247)</sup> Bulk copolymerization produces mainly insoluble polymer. Copolymerizations in dioxane or cyclohexanone, where the solvent concentration is at least 25%, produces copolymers that are 100% soluble in polar solvents.

The low-molecular-weight, soluble copolymers, produced in dioxane or cyclohexanone at 80°C, contain MA in a 1:1 or 2:1 mole ratio, depending on the monomer feed composition. With a large excess (5:1) of dicyclopentadiene 1:1 copolymer is produced. A 2:1 MA–dicyclopentadiene copolymer is formed at higher temperatures (155°C) and/or in the presence of excess MA.<sup>(263)</sup>

On the basis of polymer compositions, IR and NMR analysis, and the fact that the 1 : 1 copolymer is unsaturated and the 2 : 1 copolymer is saturated, repeating units **57** and **58** are suggested to be representative of the respective materials.<sup>(263)</sup>


**57**

**58**

Two derivatives of dicyclopentadiene, i.e., 3-isopropylidene dicyclopentadiene **59** and its 9,10-dihydro derivative **60** undergo spontaneous alternating copolymerization with MA.<sup>(240)</sup> In both cases, equimolar copolymers are produced.

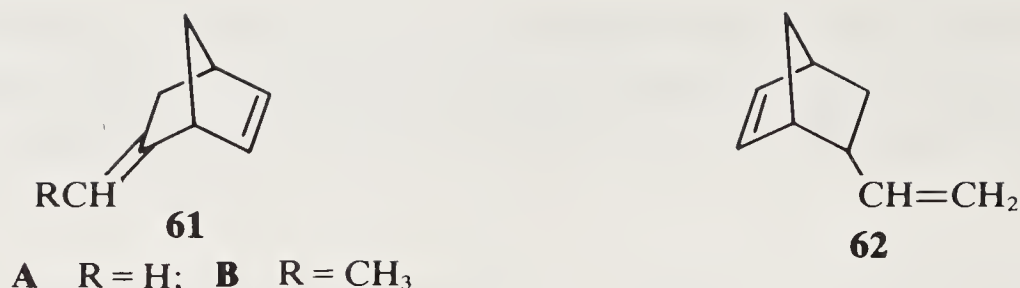

**59**

**60**

When heated in toluene for 48 h at 60°C, the yellow-colored, equimolar solutions of **59** or **60** with MA give approximately 40% yield of copolymer. Chloroform solutions (0.5 g/100 ml, 30°C) of the copolymer from **60** and MA had an intrinsic viscosity of 0.31 dl/g. In contrast, the copolymer from **59** is largely insoluble in all solvents, even when formed with free-radical initiators.

A perfectly alternating copolymer is claimed for the **60**–MA material, prepared with or without radical initiators and over a large range of monomer feed compositions. Both the yield and intrinsic viscosity values reached a maximum at equimolar feed composition. The conversion-time curves, using 1 : 1 monomer feed ratios and different polymerization temperatures, approximated straight lines. Data from the Arrhenius plot gave an activation energy of 16.8 kcal/mol,<sup>(240)</sup> comparable to an activation energy of 17.0 kcal/mol determined for the thiophene–MA comonomer pair.<sup>(264,275)</sup> Based on composition, IR, NMR, and clear evidence of a **60**–MA CTC, the strong tendency for 1 : 1 alternating copolymerization was attributed to a 1 : 1 CTC.<sup>(240)</sup>

Copolymerization of 5-methylenebicyclo[2.2.1]-2-heptene **61A**,<sup>(267–269)</sup> 5-ethylidene-bicyclo[2.2.1]-2-heptene **61B**,<sup>(227,266,269)</sup> and 5-vinylbicyclo[2.2.1]-2-heptene **62**<sup>(227,269–271)</sup> with MA is readily achieved with free-radical initiators to give equimolar copolymers.



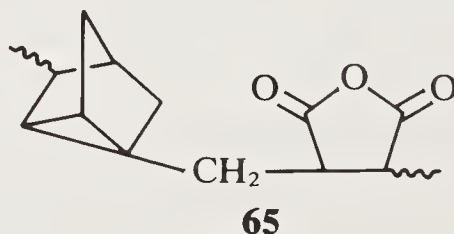


In comparison, bicyclo[2.2.1]-2,5-heptadiene (2,5-norbornadiene) **63** in the presence of free-radical initiators gives only nonalternating polymer with suggested nortricyclene residues **64**.<sup>(267)</sup>



In the earliest work,<sup>(267)</sup> various mixtures of **61A** and MA were found to copolymerize to give high yields of constant composition (1:1) materials having varying solubilities, degree of crosslinking, and molecular weights. Regardless of conversion or initial comonomer feed ratios, the copolymers were nearly always 1:1 and the results were independent of the rate of copolymerization. Solvent dilution and initiator concentration changes only affected the rate of copolymerization and molecular weight but had no effect on the copolymer composition.

On the basis of the available evidence at that time, and knowledge that the nortricyclene structure had been proposed for the 2,5-norbornadiene-sulfur dioxide copolymer,<sup>(272)</sup> it was suggested that the **61A**-MA copolymer also contained nortricyclene residues **65**, arising from an intramolecular cyclization step in the propagation mechanism.<sup>(267)</sup>

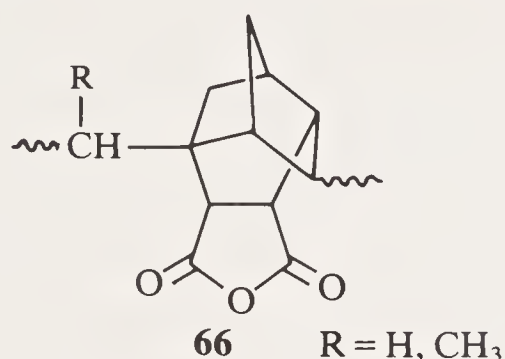


Additional work,<sup>(269)</sup> comparing the copolymerization of both **61A** and **61B** with MA, failed to substantiate the thought that a nortricyclene moiety was part of the copolymer structures.

Using a variety of solvents, different initiators, a wide range of comonomers feed ratios, and conducting the polymerizations up to 90°C, copolymers were obtained that contained MA and one or other of the dienes **61A** or **61B** in a constant (0.98:1.03) ratio. Number average molecular weights of 980–6 630, melting point range of 197–215°C, and yields in some cases of 100% were observed. It was also observed that in both cases the molecular

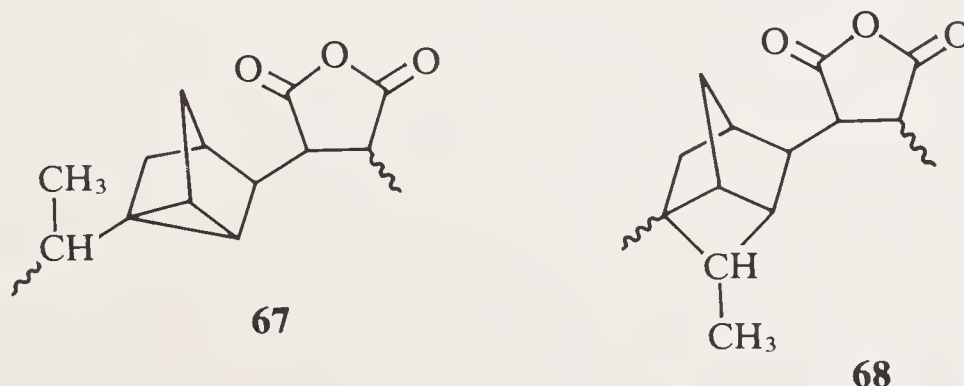
weights increased as the mole fraction of MA in the feed increased, suggesting that the two diene monomers are involved in some manner in the termination step. Under comparable copolymerization conditions, **61B**, which has two internal 1,4 double bonds, copolymerizes at a much slower rate than **61A** with MA.

Contrary to what is expected and generally observed, the slowest rates of copolymerization of **61A** and **61B** with MA was observed at equimolar feed ratios. No evidence was uncovered to support the presence of a CTC.<sup>(269)</sup>



Based on this additional information, a revised initiation and propagation mechanism was offered to account for the **61A**- and **61B**-MA copolymer structure **66**. As shown, MA is envisioned as being incorporated as part of a six-membered bicyclic structure **66** along the backbone of the polymer molecule.<sup>(269)</sup> The Pledger and Butler<sup>(269)</sup> study does not exclude the chance that a small amount of nortricyclene structure could still be part of the **61A**- or **61B**-MA copolymers.

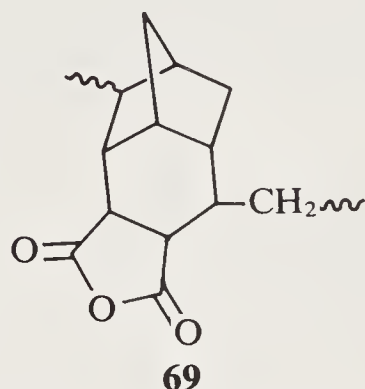
With the intent to better resolve the structure of the 5-ethylidene-bicyclo[2.2.1]-2-heptene **61B** copolymer with MA, others also looked at copolymerizations of this monomer pair.<sup>(227,266)</sup> After studying the structure of the copolymer, prepared with BPO in dioxane at 60°C, alternate structures were suggested for the material. Since the copolymers contained 50 mol % MA, homopolymerization of both monomers was excluded, and IR and NMR suggested the presence of only ethylidene double bonds and ethylidene residues, structures **67** and **68** were assumed to also be possible for the copolymer.<sup>(273)</sup>



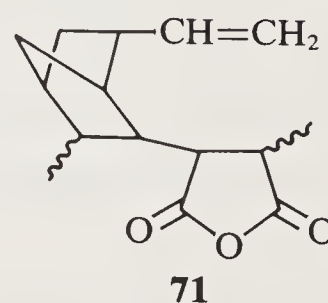
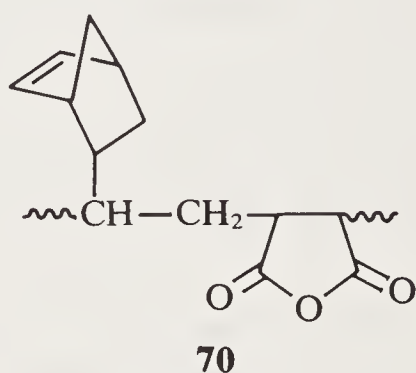
Copolymerizations under identical conditions show that ethylidenebicyclo[2.2.1]-2-heptene **61B** has a greater reaction rate, by perhaps a factor

of 3, than 5-vinylbicyclo[2.2.1]-2-heptene toward MA. It is not clear what accounts for the difference, **61B** > **61A** > **62**, in the reaction rates between the three monomers.<sup>(227,266,269)</sup>

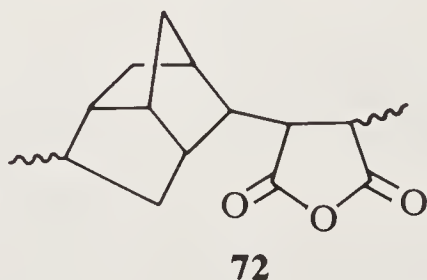
On the basis of IR and NMR spectra and composition, structural unit **69** was first considered to best represent the copolymer prepared from 5-vinylbicyclo[2.2.1]-2-heptene and MA.<sup>(269)</sup>



It was also thought that structural units **70** and **71** could also be present in the copolymer.<sup>(269)</sup>



Additional studies clearly show that the 5-vinyl group on norbornene exhibits considerably lower reactivity toward copolymerization with MA than the norbornene double bond, probably due to strong ring strain.<sup>(227,269)</sup> Considering this and other data, structure **71** is now believed to be most representative of the copolymer. It is also thought that the copolymer contains small amounts of structure **72**.<sup>(273)</sup> Additional work needs to be done before the mechanisms of these unique copolymerizations are completely clarified.



#### 10.2.15. Styrene

Among all the free-radical polymerizable monomers, highly electron-deficient MA is one of the most reactive in copolymerization with electron-rich



styrene. Since the initial patents relating to the equimolar copolymerization of styrene with MA issued,<sup>(275–278,334)</sup> considerable work has been reported on the copolymerization of this monomer pair.<sup>(20,21,57,60,66,141,279–314,1021,1034,1044,1049,1076)</sup> Alfrey and Lavin<sup>(279)</sup> were among the first to study this system and show that alternating copolymers, having number average molecular weights of 1 300–10,000, could be obtained with common free-radical initiators at 70–80°C polymerization temperatures. Melville and Burnett<sup>(233)</sup> estimated the rate constant for the copolymerization at 25°C to be 505 liters mol<sup>-1</sup> s<sup>-1</sup>.

For the most part, since the early 1940s, the free-radical-initiated copolymerization of styrene with MA has been regarded as one of the best examples of an alternating copolymerization system.<sup>(315)</sup> For that reason, this has probably been the most investigated and discussed of the classical alternating copolymerizations. Various derivatives of MA, such as dialkyl fumarates and maleimides, are also known to have a strong tendency to undergo equimolar copolymerization with styrene. Using inert solvents, attempts are currently being made to better understand the lack of good copolymerizability between styrene and dialkyl maleates.<sup>(1078)</sup>

The following general remarks apply to copolymerization of this monomer pair. Where polymerizations are run in a large excess of styrene, some polystyrene is formed along with alternating copolymer. The ratio of monomers in the feed may be varied but it can be shown, by both chemical and physical analyses, that the styrene and MA are present in the copolymer in equimolar ratio when MA is present at the start of the reaction in equimolar or excess amounts. The copolymerization reaction is strongly exothermic and must be controlled by proper selection of initiator, use of appropriate solvents, and/or regulation of temperature. Exposure of styrene to oxygen during storage or immediately before polymerization accelerates the rate of copolymerization, due to polystyrene peroxide formation.<sup>(1043)</sup> The induction period decreases with increasing oxygen content in the system, with the polymerization rate increasing sharply at first and then more slowly as high oxygen levels are reached. Raetzsch *et al.*<sup>(1060)</sup> feel the rate increase, due to oxygen, cannot be explained by the formation of polymeric peroxy compounds. In attempting to explain the oxygen effect, they discuss a reaction mechanism involving a cationic styrene radical and an anionic MA radical.

The styrene–MA copolymerization reactions are usually conducted at temperatures in the range 40–100°C, with peroxide initiators and hydrocarbon solvents.<sup>(275–278,292,324–334)</sup> It is known that equimolar mixtures of the two monomers will readily undergo spontaneous copolymerization at 80°C to give alternating copolymer.<sup>(327)</sup> The copolymers are usually insoluble in the polymerization solvent and precipitate as fine powders. The use of ketone-type solvents leads to a viscous solution of copolymer which can be isolated by addition of a nonsolvent. To control the exothermic reaction, polymerizations

are often run at approximately 20% solution.<sup>(276)</sup> Chronoconductometric techniques may be used to determine free MA in the copolymers.<sup>(321)</sup>

Tamura *et al.*<sup>(1055)</sup> recently investigated the hydrogen isotope effect on the spontaneous copolymerization of styrene with MA in various solvents. The spontaneous copolymerization of several deuterated styrenes and a perdeuterated MA, in solvents such as toluene, ethylbenzene, cumene, or *p*-cymene at 60°C, showed a decrease in overall copolymerization for styrene-2,4,6-*d*<sub>3</sub> with MA and for styrene with perdeuterated MA, compared with that of styrene with MA in the same solvent. The results showed that hydrogen abstraction from the *ortho* position of styrene and from MA could be important in initiation. Also hydrogen abstraction from solvents, with a labile hydrogen in  $\alpha$  position, plays a role in initiation.

Similar to the situation observed for the vinyl acetate-MA copolymerization,<sup>(155)</sup> as copolymerization temperatures increase above 80°C for the styrene-MA pair the polymers become more and more random. Copolymerization at 180°C in bulk or 130°C in decalin produces only random copolymer.<sup>(305,309,310)</sup> Instability or absence of charge-transfer complexes is believed to account for the shift to statistical-type copolymerization.

Styrene-MA type polymers were introduced in this country by Sinclair petrochemicals in the early 1960s (see Sec. 10.6.1). Monsanto and Arco Chemical with their Lytron and SMA resins, respectively, are commercial merchant producers of these resins. Others, such as Dow Chemical, Deering-Milliken, etc., produce these resins for their own use. The low-molecular-weight, 1 600–2 200, SMA resins marketed by Arco Chemical Company are white powders, soluble in acetone and also methyl alcohol or dilute alkali by alcoholysis or hydrolysis, insoluble in hydrocarbon solvents, and exhibiting a softening range for the 1 : 1 copolymer at 150–170°C. The Monsanto Lytron resins have a much higher molecular weight, 10,000–50,000, and are usually supplied as a monoalkyl ester.

Copolymers of styrene and MA are conveniently prepared commercially by a precipitation processes, usually in aromatic hydrocarbons. Depending on monomer feeds, the copolymer may differ from 1 : 1 alternating. Filtration and drying affords the products in powder or granule form.<sup>(328)</sup> Low-molecular-weight products may be obtained from reactions in highly alkylated aromatic hydrocarbons, such as *p*-cymene.<sup>(329)</sup> Also, alkylmercaptan chain regulators in diethylbenzene are useful to reduce molecular weight.<sup>(330)</sup> High-molecular-weight copolymers with high bulk density can be prepared with active initiators such as diisopropyl peroxycarbonate or *tert*-butyl peroxyphthalate.<sup>(331)</sup> Solution processes, which provide powder products, are usually run in ketone solvents under pressure<sup>(332)</sup> or continuous feed and takeoff in an extruder.<sup>(333)</sup> Good quality control may be achieved by running the copolymerization in *N,N*-dimethylacetamide or dibutyl ether solvents at 105–120°C.<sup>(1029)</sup> A recent suspension copolymerization process has also been



developed to prepare finely divided powder with a relatively uniform particle size.<sup>(197)</sup> The method employs novel macromolecular dispersing agents, which are soluble in aliphatic hydrocarbons and are prepared from alternating copolymers of MA.

Using AIBN initiator and copolymerizing the styrene–MA monomer pair in *o*-dichlorobenzene at 60°C, it was shown that on changing from a homogenous to a heterogeneous system the reaction rate is enhanced, i.e., autoacceleration was observed with no apparent change in reactivity ratio.<sup>(280,281)</sup> For the condition  $[MA]/[styrene] < 1 \times 10^{-2}$ , approximately, on a molar basis, the polymer remains in solution, but at higher ratios it precipitates in a somewhat swollen form. At the critical value of  $[MA]/[styrene]$  a discontinuity in the kinetic behavior occurs. In addition, where the polymer precipitates during polymerization the rate of reaction increases with time and the initiator exponent in the rate equation is  $>0.5$ . This may be attributed to a reduction in the termination rate ( $k_t$ ) values, occurring when the polymer fails to remain dissolved in the reaction medium. Evidently moderate occlusion maintains monomer availability. A constant rate and an exponent of 0.5 is normally observed for homogeneous systems. In contrast, heterogeneous copolymerization of the pair in decane tends to increase the amount of anhydride in the co-polymer.<sup>(283)</sup> For this condition, it is speculated that the anhydride is highly associated in such solvents and readily absorbed on the growing polymer molecule, resulting in easier incorporation. Tsuchida and coworkers,<sup>(291)</sup> in comparing the rates of copolymerization in solution and the precipitation processes, confirmed the Bamford and Barb<sup>(280)</sup> observation. They also found that the rates are much faster for the heterogeneous system, but the composition of the copolymers remain equimolar, whatever the medium.

Solution copolymerization of the monomer pair in acetone or cyclohexanone at 50 or 100°C, with AIBN, produced the following results. At 50°C, the reaction starts to occur after about 6 h and yields of 0, 30.5, 51.8, 67.4, and 69.7% are obtained after 6, 8, 10, and 12 h, respectively. Regardless of the time and temperature, up to about 120°C, and at equimolar or excess MA feed ratios, the resultant copolymers are 1 : 1 alternating.<sup>(284)</sup>

Seymour *et al.*<sup>(285)</sup> and Tsang<sup>(16)</sup> studied the role of solubility parameters ( $\delta$ ) in the copolymerization of MA with vinyl monomers. The rates of copolymerization of the styrene–MA pair are shown to be much slower in acetone solution than in heterogeneous systems. Rates in the heterogeneous systems decreased as the solubility parameters decreased from xylene ( $\delta = 8.82$ ) to *p*-cymene ( $\delta = 8.2$ ). Rates were greatest in benzene solvent. It is assumed that the rates were greatest under heterogeneous conditions because of the lesser probability of termination by coupling or disproportionation of radical chain in poor solvents. Again, moderate occlusion of monomer in the precipitated growing polymer maintains high polymerization rates.



Kinetic studies of the copolymerization in acetic anhydride, using a dilatometric technique, showed that the order of the reaction with respect to the product of the monomer concentrations is close to 0.5. Also, the rates were slightly enhanced as MA concentrations were increased. This tends to indicate that the alternating copolymerization occurs by successive addition of the monomers.<sup>(286)</sup>

Solution copolymerization of the MA–styrene pair has been studied in acetone at high pressure (1–4 kbars). At 40°C, the copolymerization reaction rate between MA and the growing polymer chain, having a MA unit preceding the active styrene moiety, increased with pressure for both bulk and solution copolymerizations condition. Thus, Enomoto and coworkers<sup>(299)</sup> conclude the penultimate effect diminishes or disappears with pressure escalation. Composition and infrared studies show a 1 : 1 alternating structure for the material, over a wide range of monomer concentration of one component.

Using filtered light from a mercury–quartz lamp, photochemical polymerizations have been studied for both bulk and solution systems.<sup>(66,685,1021,1044,1045,1054,1062,1116)</sup> Polymerization in benzene or acetone for 3 h gave copolymer having intrinsic viscosities in THF of 1.10–3.55 dl/g (0.5 g/100 ml, 25°C). Bulk copolymerization, with 10 mol % MA in styrene monomer, gave equimolar copolymer with intrinsic viscosity of 1.62 and molecular weight by light scattering of 450,000. In looking at other solvents, it was discovered that photochemical copolymerizations would not occur in DMF. Using dioxane solvent, it was found that copolymer molecular weight decreased with increasing amounts of MA in the feed. Also, rates of copolymerization increased and molecular weights dropped as the concentration of dioxane in the comonomer mixture solution increased.<sup>(1021)</sup> The rate of polymerization in acetone, tetrahydrofuran, and acetonitrile passed through a maximum with increasing proportion of MA in the monomer mixture, with the maximum being shifted to higher MA content with increasing overall monomer concentration. In dioxane the rate increased monotonically with increasing proportion of MA. The molecular weight of the product passed a maximum with increasing proportion of MA for polymerization in acetonitrile and dioxane and increased with increasing proportion of MA for polymerization in acetone. Addition of benzophenone as a photosensitizer, in the presence of acetone solvent, increases the rate of polymerization and decreases the polymer molecular weight.<sup>(1034)</sup> The dependence of rate on the concentration of 1 : 1 mixture of monomers in acetone suggests that a styrene–acetone exciplex is involved in initiation. The reaction order with respect to monomer varied with monomer ratio and donor strength of the solvent.<sup>(685)</sup>

Attempts have been made to prepare optically active styrene–co–MA materials using polarized  $\beta$  radiation<sup>(300)</sup> and copolymerization in the presence of lecithin.<sup>(789)</sup> Equimolar copolymer was readily obtained using  $\beta$  radiation, but no optical activity was detected in the copolymer. In contrast, the chirality

of lecithin induced optical activity into the backbone of the styrene-MA copolymer. The observed specific rotation of the resulting alternating copolymer decreased with an increase in the dielectric constant of the solvent used for polymerization. The authors concluded that the asymmetric induction depends mainly upon the incorporation of MA within the reversed lecithin micelles.<sup>(789)</sup> Copolymerization of equimolar mixtures in *l*-methanol, with AIBN, is also known to produce optically active copolymer, with  $\bar{M}_n = 15,300$  and optical rotation  $[\alpha]_D^{25}$  of +0.36 to 0.44.<sup>(373)</sup> It is also known that copolymerization of (-)-3-menthyl hydrogen maleate with styrene produces optically active copolymer, even after removal of the (-)-3-menthol group by hydrolysis.<sup>(556)</sup>

In the presence of zinc or barium sulfide, mixtures of styrene and MA undergo radical copolymerization by mechanical force.<sup>(307)</sup> Addition of standard free-radical inhibitors prevented copolymerization and established the free-radical nature of the polymerization system. Maximum copolymer yields were obtained for an equimolar mixture after a 100-min dispersion. Others have also studied the solid-phase mechanochemical copolymerization of MA with styrene.<sup>(308)</sup> The CTC formation in the system was confirmed spectrophotometrically.

Several organometallic compounds, such as trialkylaluminum<sup>(57)</sup> and metal chelates of acetylacetonate,<sup>(289)</sup> are known to initiate copolymerization of MA with styrene. In the presence of trioctylaluminum, mixtures of MA and styrene undergo spontaneous copolymerization to yield alternating copolymer. The copolymerizations are inhibited by diphenylpicrylhydrazyl. While studying the solution copolymerizations under argon, it was found that the polymerizations were initiated by paramagnetic centers being generated. Structure 9 (Sec. 10.2.2) illustrates the MA-bis(trioctylaluminum) complex believed to initiate copolymerization.<sup>(57,154)</sup>

The copper II chelate of acetylacetonate is also an effective initiator for styrene-MA copolymerization.<sup>(289,290)</sup> In acetone at 60°C, copolymerizations progress readily to give 1:1 alternating material. The copolymers appear to be essentially the same as those prepared with peroxide initiators. Activity varies with the central metal atom of the chelate and follows the order  $\text{Mn}^{3+} \geq \text{Fe}^{3+} \geq \text{Co}^{3+} > \text{Cr}^{3+} > \text{Ni}^{3+} > \text{Cu}^{2+}$ .

The effects of adding nonpolymerizable and polymerizable electron donors, such as anthracene, naphthalene, cyclohexene, and dihydrofuran, to the styrene-MA copolymerization system has received substantial study by Tsuchida and coworkers.<sup>(293,295)</sup> The ability of these additives and styrene to complex with MA follows the order anthracene > naphthalene > styrene > cyclohexene > dihydrofuran. Naphthalene addition reduced the overall activation energy, increased the rate of thermal initiation and propagation slightly, and increased the rate of copolymerization. In addition, the rate maxima shifted from compositions poor in styrene toward equivalence. Because



a polymerization accelerating phenomenon was observed in the system containing naphthalene, a decline in the apparent activation energy ( $E_A$ ) was predicted. Measuring the variation of rate ( $R_p$ ) with temperature and interpretation of the results showed the anticipated drop in activation energy.

- Styrene-MA (benzene), 16.02 kcal/mol
- Styrene-MA-naphthalene (benzene), 15.76 kcal/mol
- Styrene-MA-(tetrahydrofuran), 18.60 kcal/mol
- Styrene-MA-naphthalene (tetrahydrofuran), 17.31 kcal/mol

The molecular weights of the copolymer prepared in the presence of naphthalene, in both the benzene and THF solvents, were lower than the corresponding copolymer prepared without naphthalene. The decline is attributed to chain-transfer reactions.<sup>(293)</sup> From other copolymerization studies, in the absence of additives, it has been concluded the activation energy was 12.8 kcal/mol.<sup>(294)</sup>

Both dihydrofuran and cyclohexene function to lower the rate of copolymerization of styrene with MA. However, the effect of cyclohexene is not as pronounced since it mainly functions as a diluting agent, whereas, the rate decline is proportional to the amount of dihydrofuran additive. A striking decline in rate is observed when anthracene is added. This is probably due to temporary inhibition of polymerization in which anthracene acts as a radical trap and Diels-Alder reactions (see Chapter 4) occur.

In contrast to naphthalene, the presence of DMA significantly affects the composition of the styrene-MA copolymers.<sup>(295,297)</sup> Dimethylaniline forms a CTC with MA (see Table 10.15, Sec. 10.4) and by both a degradative and effective chain-transfer effect, systems with DMA present have enhanced amounts of MA in the copolymer. The DMA-MA CTC is capable of generating radicals and initiating free-radical polymerization of vinyl monomers.<sup>(295)</sup> It has also been reported that an amide-MA CTC will initiate polymerization of styrene.<sup>(67,481)</sup>

Styrene-co-MA polymer end groups have been studied by a tracer method, using  $^{14}\text{C}$ -labeled AIBN as an initiator and activation analysis.<sup>(296)</sup> Initiation occurs by an attack on the monomer or the CTC of initiator radicals, and then a violent chain transfer to the monomer or CTC occurs during the alternating copolymerization. Chain transfer to  $\text{CCl}_4$  was shown to be of no importance.

When a CTC, such as styrene-MA, is undergoing copolymerization, the system can initiate the polymerization of other vinyl monomers, such as a styrene-methyl methacrylate pair.<sup>(327)</sup> In contrast, the CTC formed between the styrene-MA copolymer and styrene will not initiate the homopolymerization of styrene.<sup>(1046)</sup> Experimental results tend to support the thought that a polymerizing or activated styrene-MA CTC initiates the polymerization. The initiation of free-radical copolymerization by a polymerizing CTC has also been claimed for the *N*-vinylpyrrolidone-methyl methacrylate-MA

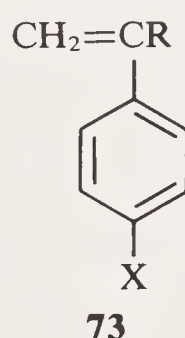


system.<sup>(169)</sup> Also, the propagating styrene-MA chain can be used to initiate homopolymerization of styrene to obtain a block copolymer, consisting of an alternating styrene-co-MA block and a polystyrene block.<sup>(335)</sup> Seymour *et al.*<sup>(336-340)</sup> have extensively investigated and used styrene-co-MA macroradicals to prepare block copolymers. The alternating copolymer macroradicals, prepared under heterogeneous conditions, exhibited long-term shelf life in oxygen-free atmosphere at  $-20^{\circ}\text{C}$ . Various vinyl monomer polymerizations were initiated with the macroradicals.

Alternating styrene-co-MA polymer has been grafted on polyethylene, polybutadiene, and polystyrene.<sup>(335,341,342,1053)</sup> For example, heating a benzene solution of polystyrene and an equimolar mixture of styrene and MA at  $60-80^{\circ}\text{C}$  for several hours produces the aforesaid grafted material (see Chapter 11). An equimolar mixture of styrene and MA may also be heated at  $120^{\circ}\text{C}$  with polyethylene to initiate spontaneous copolymerization and grafting, to obtain carboxylated polyethylene.<sup>(341)</sup> The low-molecular-weight polybutadiene, prepared with sodium catalyst, was treated with equimolar amounts of styrene and MA in dioxane solvent with AIBN initiator. Alternating styrene-MA branches were detected in the product, with grafting increasing with time.<sup>(1053)</sup>

### 10.2.16. Substituted Styrenes

A variety of substituted styrenes **73** have also been shown to undergo alternative copolymerization with MA.<sup>(13,17,181,187,342-347,352,1061)</sup>



$\text{R} = \text{H}, \text{CH}_3$ ;  $\text{X} = \text{none}, \text{CH}(\text{CH}_3)_2, \text{OCH}_3, \text{N}(\text{CH}_3)_2, \text{Cl}, \text{Br}, \text{I}, \text{F}, \text{CN}, \text{and } \text{NO}_2$   
 $\text{R} = \text{H}$ ;  $\text{X} = \text{CH}_2\text{Cl}, \text{CH}_2\text{Br}, \text{and } \text{N}(\text{CH}_3)_2$

Over a wide range of monomer mixtures and using typical free-radical initiators or radiation-induced methods,  $\alpha$ -methylstyrene **73** ( $\text{R} = \text{CH}_3, \text{X} = \text{none}$ ) will copolymerize with MA to give 1:1 alternating materials.<sup>(342-345,476,1061,1087)</sup> Copolymerizations may occur even without added initiators.<sup>(343)</sup> A typical copolymer, prepared with radical initiators in decalin at  $80^{\circ}\text{C}$ , has a polymer melt temperature of  $210^{\circ}\text{C}$ .<sup>(476)</sup>

Peroxide-initiated, bulk copolymerization of MA with trifluoromethyl-, halo-trifluoromethyl-, halogen-, halo-alkyl-, etc., substituted styrene and  $\alpha$ -methylstyrene monomers at  $65-70^{\circ}\text{C}$ , were studied briefly by Backman and

coworkers.<sup>(118)</sup> Little is known about the structure of these MA-containing copolymers, but it is assumed they were equimolar since 1 : 1 feeds were often used to prepare the materials.

Radiation-initiated copolymerizations, either bulk or in solution, exhibit no induction period for the  $\alpha$ -methylstyrene–MA monomer pair. Standard free-radical inhibitors prevent or stopped the copolymerizations. Apparent activation energies of 6.7 and 5.4 kcal/mol were obtained for the bulk (3.6 mol % MA in  $\alpha$ -methylstyrene) and (8.0 wt. % chloroform solution of equimolar amounts of the monomer pair) copolymerizations, respectively. Composition and IR spectra studies indicated that homopolymerization of either of the two monomers did not occur, under conditions explored, and that alternating copolymerization occurred over a wide range of monomer concentration of one component.<sup>(344)</sup> As pressures are raised from 1 bar to 3 bars, considerably enhanced rates of copolymerization are observed.<sup>(187)</sup> Above 80°C random copolymer is obtained.<sup>(476)</sup>

The striking feature of the free-radical-initiated alternating copolymerization of substituted  $\alpha$ -methylstyrenes **73** [ $R = CH_3$ ;  $X = OCH_3$ ,  $N(CH_3)_2$ , etc.] is the enhanced (high) reactivity of the dimethylamine, methoxy, and methyl substituted monomers toward the MA radical.<sup>(17,346)</sup> The increased reactivity of the  $-N(CH_3)_2 \gg -OCH_3 > -CH_3$  monomers parallels the capacity of those substituted styrenes to form colored charge-transfer complexes with MA and appears to increase with the “alternating tendency” of the monomers from which the attacking radical was derived.<sup>(17)</sup>

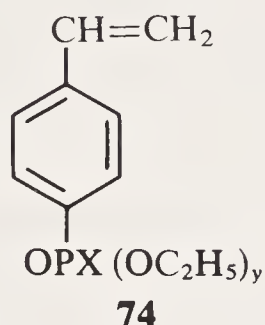
The free-radical copolymerization of *p*-isopropyl- $\alpha$ -methylstyrene has been studied in chloroform solvent at 60°C, with BPO initiator.<sup>(1061)</sup> Copolymerization gave a 1 : 1 copolymer regardless of the feed ratios, with the highest rate of copolymerization being obtained at equimolar feed. Kinetic studies at 1 : 1 feed and various concentrations of BPO showed an order of 1.07 and 0.65 with respect to the concentrations of MA and BPO. The overall activation energy was of the order of 7.6 kcal/mol. The dependence of copolymerization rate on monomer concentration and feed ratio shows that the mechanism of copolymerization cannot be simply explained by the participation of charge-transfer complexes formed between the two monomers.

The relative reactivities of all  $\alpha$ -methylstyrenes toward the MA-type radical fails to relate to the Hammett sigma values<sup>(351)</sup> for the substituents, contributing support to the thought that special resonance structures in the reaction contribute to the driving force for the alternating copolymerization.<sup>(17)</sup>

Furukawa *et al.*<sup>(349)</sup> prepared styrene monomers containing phosphorus substituents **74** and studied copolymerization of these compounds with MA. Copolymerizations were run at 60°C in toluene, with AIBN initiator. In all cases, elemental analysis showed the low-molecular-weight copolymers exhibited equimolar composition. The copolymers are being examined as chelating agents for various metal ions.



Free-radical-initiated copolymerization of *o*-phenylstyrene with MA has been briefly examined.<sup>(350)</sup> It is assumed that the copolymer, prepared neat at 80°C with BPO initiator, was equimolar. The melt temperature (pmt) for the copolymer was 235–240°C.

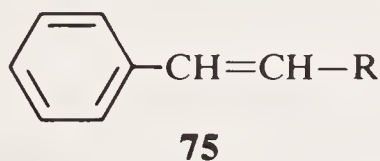


X = O or S, y = 2

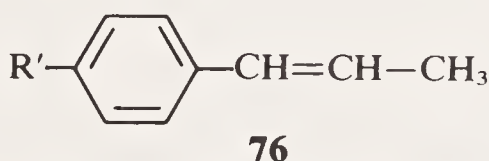
X = OCl or SCl, y = 1

### 10.2.17. Stilbene and Other Aromatic Monomers

In addition to stilbene<sup>(3,87,353–356,1134)</sup> and 1,1-diphenylethylene,<sup>(187)</sup> several other  $\beta$ -substituted styrenes, **75** and **76**, have also been reported to undergo equimolar copolymerization with MA.<sup>(87)</sup> For the case where the  $\beta$ -substituent (R) on the monomer **75** is an alkyl ether (R = OCH<sub>3</sub>, OC<sub>2</sub>H<sub>5</sub>, etc.) **10**, residue, the subject was reviewed earlier<sup>(87,88)</sup> in Sec. 10.2.2.



R = C<sub>6</sub>H<sub>6</sub> (*cis* and *trans*), CH<sub>3</sub>,  
CO<sub>2</sub>CH<sub>3</sub>, Cl, and COCH<sub>3</sub>



R' = CH<sub>3</sub>O, CH<sub>3</sub>, H, and Cl

Spontaneous copolymerization of stilbene–MA occurs in refluxing xylene mixtures to give insoluble product. This was the first case reported in the literature where two monomers, both of which are resistant to homopolymerization, could be combined and copolymerized to give equimolar copolymer.<sup>(3)</sup> A number of additional studies have since shown that copolymerization of various mixtures of this monomer pair can also be achieved with standard free-radical initiators<sup>(8,353,355,357)</sup> or ultraviolet radiation<sup>(354)</sup> to obtain essentially 1 : 1 copolymer.

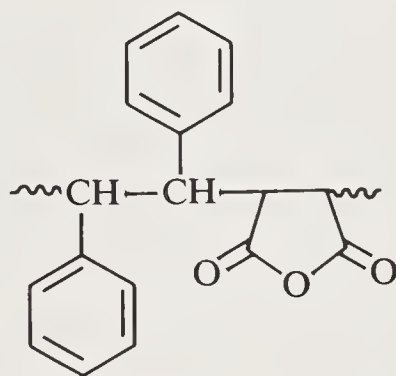
Using both BPO and AIBN initiators and different solvents, rate data show that *trans*-stilbene is at least 1.5–2 times as reactive as the *cis*-stilbene toward the MA radical.<sup>(87,353)</sup> Also, *trans*-stilbene is markedly less reactive than styrene toward MA.

*Trans*-stilbene–MA copolymerizations have also been run in both chloroform and THF from 1 bar to 3 200 bars, using lauroyl peroxide at 70°C. At 1 bar, the maximum yield of 75% was obtained after about 30 h. In contrast, at 3 200 bars the maximum yield of 75% was obtained in only 8 h. The copolymerization volume calculations supported the thought that a



compact transition state exists during copolymerization, in agreement with the possible existence of a penultimate effect for MA-rich feeds.<sup>(187,355)</sup> Soluble copolymers exhibited a weight average and number average molecular weight, respectively, of 5 700 and 1 080. The copolymer exhibits strong fluorescence emission<sup>(356,357)</sup> and starts to decompose at about 300°C,<sup>(355)</sup> compared to copolymer softening temperatures of >300°C and 230–250°C previously reported<sup>(87)</sup> for the *trans*-stilbene and *cis*-stilbene–MA copolymers, respectively.

No copolymerization of the *trans*-stilbene–MA mixture occurs when kept in the dark for 48 h. However, monomer mixtures in both acetone and THF slowly copolymerize on exposure to 3 500-Å light at 0 or –78°C.<sup>(354)</sup> The polymer compositions were consistent with a 1 : 1 comonomer ratio and NMR confirmed structure **77**.

**77**

The molecular weight of the copolymer **77** was low and independent of conversion. The presence of several photosensitizers had no great effect on the rate of polymerization. Only the presence of benzil, which generates free-radicals upon irradiation, increased the conversion.<sup>(354)</sup> At conversions in excess of 7–10% only insoluble polymer was generated, which also occurs in both the spontaneous and free-radical-initiated copolymerizations.

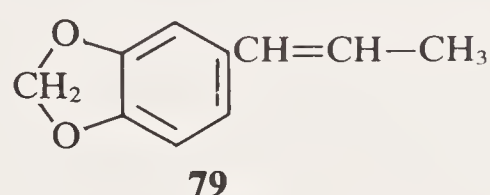
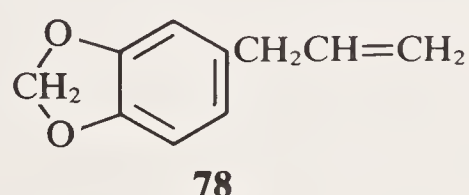
The free-radical-initiated copolymerization of *trans*-stilbene with MA was recently studied as a route to poly(methyl cinnamate).<sup>(357)</sup> Alternating copolymers were prepared with specific viscosities, measured at 30°C in 0.5 NaOH (0.2 g/100 ml), as high as 1.40 dl/g. Esterification with methyl alcohol gave head-to-head (H-H) poly(methyl cinnamate). Even though H-H poly(methyl cinnamate)  $T_g$  was higher than head-to-tail (H-T) poly(methyl cinnamate), the H-H material had poorer stability than the H-T material.<sup>(199,200)</sup>

All the other  $\beta$ -substituted styrenes **75**, similar to *cis*- and *trans*-stilbene, were also markedly less reactive than styrene with MA. Rates of copolymerization at 60°C in benzene, with AIBN initiator, were found to decrease approximately with the increase in electron-attracting characters of the  $\beta$  substituents, e.g.,  $\text{OCH}_3 > \text{CH}_3 > \text{CO}_2\text{CH}_3 > \text{Cl} > \text{COCH}_3$ .<sup>(87)</sup> For the copolymerization of *para*-substituted  $\beta$ -methylstyrene **76** in benzene at 60°C

with AIBN, rates followed the order  $\text{CH}_3\text{O} \gg \text{CH}_3 > \text{H} > \text{Cl}$ .<sup>(87)</sup> The *para*-substituents  $\text{CH}_3\text{O}$ ,  $\text{CH}_3$ ,  $\text{H}$ , and  $\text{Cl}$  had little or no effect on copolymer compositions, i.e., all tended to be 1:1 regardless of monomer feed ratios. Rates of copolymerization generally increased with an increase in the fraction of MA, sometimes showing a maximum. The studies clearly suggest that both steric and polar, as well as resonance forms, may give rise to rather complex  $\beta$ -substituent effects.<sup>(87)</sup>

Aromatics with propenyl and isopropenyl residues also undergo equimolar copolymerization with MA.<sup>(46,345,358–362)</sup> Anethole (*para*-propenylanisole) and *ortho*-propenylphenol, by analogy with the vinyl ethers, do not undergo free-radical-initiated homopolymerization but will copolymerize (1:1) with MA. Even for terpolymer systems, where anethole ( $\text{M}_1$ ) and MA ( $\text{M}_2$ ) were combined and copolymerized with  $\beta$ -chloroethyl methacrylate, methacrylonitrile or acrylonitrile (Table 10.23), the terpolymer obtained always had a  $\text{M}_1/\text{M}_2$  ratio of 1.<sup>(358)</sup> The copolymerization of *o*-propenylphenol with an equimolar amount of MA, in 2-butanone for 8 h at 70°C with 1% AIBN, gave an 81% yield of low-molecular-weight 1:1 copolymer.<sup>(46)</sup> The copolymer structure, solubility, and molecular weight are very similar to the 2-allylphenol–MA copolymer previously discussed (Sec. 10.2.1).

Using tributylborane initiator, 4-propenyl pyrocatechol **79** a derivative of isosafrole **78** copolymerizes readily with MA.<sup>(359)</sup> The copolymer contains equimolar amounts of **79** and MA, regardless of the monomer feed ratios and the materials exhibited polymer melt temperatures of approximately 270°C. Monomers **78** and **79**,<sup>(363,364)</sup> as well as *p*-allylanisole,<sup>(364)</sup> are also reported to copolymerize with MA when mixtures of the monomers are heated at 100°C in xylene.<sup>(363)</sup> Even though equimolar copolymers are claimed, the work needs reinvestigation to see if ene product (see Chapter 5) is also formed.



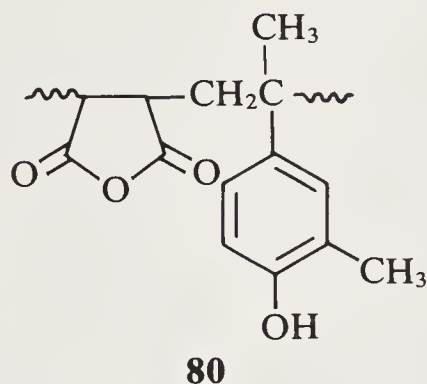
Tri-*n*-butylborane is also capable of initiating the copolymerization of 2-vinyl-1,4-hydroquinone (VHQ) with MA and diethyl fumarate to obtain alternating copolymers.<sup>(365)</sup> Copolymerization with MA in cyclohexanone at 30°C gave the VHQ copolymer in 78% yield, with an intrinsic viscosity measured in THF at 30°C of 0.16 dl/g. Differential thermal (DTA) and thermogravimetric analysis (TGA) studies show that degradation of the copolymer occurs mainly in the temperature range 300–400°C, with about 55% weight loss. The redox potential of the copolymers were examined, showing the midpoint potential of the copolymer to be higher than VHQ.

The monomers *ortho*- and *para*-isopropenylphenol<sup>(360,361,366)</sup> and  $\beta$ -isopropenylnaphthalene,<sup>(362)</sup> similar to  $\alpha$ -methylstyrene, are also reported to



copolymerize 1:1 with MA. Using AIBN or *t*-butylperoxide initiators, equimolar copolymers of *ortho*- and *para*-isopropenylphenol with MA were obtained in yields up to 96% and inherent viscosities up to 0.44 dl/g (dioxane, 25°C). The copolymers were yellow solids having a softening point in the range of 82–180°C. The *para*-isomer gave the highest yields and AIBN produced the highest molecular weight.<sup>(360)</sup> A copolymer with  $[\eta] = 0.10$  dl/g (dioxane, 25°C) is claimed to have a number average molecular weight ( $\bar{M}_n$ ) of 85 000.<sup>(366)</sup>

Equimolar copolymers of 2-methyl-4-isopropenylphenol and its methyl ether with MA are also readily obtained.<sup>(361)</sup> Heating mixtures of the two monomers in benzene with AIBN or *tert*-butylperoxide, over the range 80–140°C, gave 1:1 copolymer **80** in yields up to 95%. The copolymers briefly discussed in this section and in other sections (10.2.1 and 10.7.1), with both pendent anhydride and phenolic residues, are potentially useful in many applications.



Copolymers with alternating MA and  $\beta$ -isopropenylnaphthalene residues, prepared by AIBN-initiated copolymerization of the monomer pair in toluene, have received some study.<sup>(362,788)</sup> Copolymer compositions are independent of starting feed ratios and always essentially 1:1. As MA goes up from a 1:1 to 5:1 ratio the yields of copolymer increased from 38 to 59%. On the basis of ultraviolet studies showing a fairly strong CTC between the two monomers (see Appendix, Chapter 10) and the fact that rates were observed to increase with CTC concentration, it was proposed that a CTC played a major role in the copolymerization.<sup>(362)</sup> However, some recent results cast doubts on such claims.<sup>(1066)</sup>

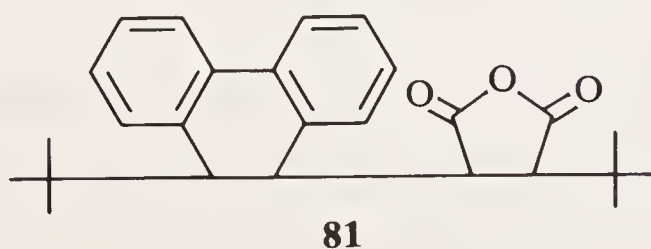
Phenanthrene,<sup>(367–369)</sup> indene,<sup>(370–372)</sup> *N*-ethyl-2-vinylcarbazole,<sup>(374)</sup> acenaphthylene,<sup>(356,357,375–379,890)</sup> and derivatives of dihydronaphthalene or dihydroacenaphthene,<sup>(380)</sup> in the presence of typical free-radical initiators, will undergo 1:1 copolymerization with MA.

Using a large number of different solvents and conducting copolymerizations at 60°C with AIBN, phenanthrene–MA copolymers with 1:1–1:1.2 molar ratios of starting monomers were obtained. Rates, molecular weights, and yields were influenced by solvents. Yields were best in dioxane, carbon tetrachloride, chloroform, acetic anhydride, dichloroethane, benzene, toluene,



and xylene. Copolymerization was not observed in DMF and only a trace in THF. Copolymer intrinsic viscosities, measured in acetone at 25°C, varied from 0.06 to 0.13 dl/g. Molecular weights, determined in acetone by the ebulliometric method, varied from 3 600 to 6 100. Rates were enhanced slightly by an increase in concentration of the CTC formed between the monomer pair.<sup>(367)</sup> In general, solvents which tended not to form a CTC with MA gave best results. Kinetic studies, run in dioxane and benzene, supported the theory that a CTC strongly controlled copolymerization. In dioxane, the maximum rate of polymerization was achieved where MA was in slight molar excess. In benzene, the maximum rate appeared at the 1:2 molar feed composition of phenanthrene: MA. Short induction periods occur for all the copolymerization, especially when excess phenanthrene was employed. The polymer obtained from precipitation in benzene or by polymerization in dioxane contained a large amount of essentially 1:1 low-molecular-weight material. In contrast, higher-molecular-weight copolymers obtained by polymerization in benzene and precipitated from methyl alcohol showed a 1:2 composition.<sup>(367,368)</sup>

Wishing to exclude the influence of solvent, Heseding and Schneider<sup>(369)</sup> studied the melt copolymerization of phenanthrene with MA, using  $^{60}\text{Co}$   $\gamma$  rays with dose rates of  $7.8 \times 10^4$ – $1 \times 10^6$  rads/h and temperatures of 80–170°C. Up to about 130°C conversions increased almost linearly with irradiation time. Greater than 130°C, the conversions approached a constant value that decreased with increasing temperature. The ceiling temperature was determined as 180°C and maximum rates were observed for about 78 mol % MA. A plot of phenanthrene mol % in the copolymer versus reaction temperature, over the range 80–160°C, showed phenanthrene content decreased somewhat with temperature elevation. The copolymers are colorless, solid materials, soluble in dioxane, THF, and acetic anhydride and insoluble in aromatic hydrocarbons. At the reaction maximum, the molecular weight of the copolymer is of the order of  $10^4$ . Infrared spectrum and composition data support structure **81** for the material prepared at 65°C in 10 h, at a dose rate of  $7.8 \times 10^4$  rads/h.



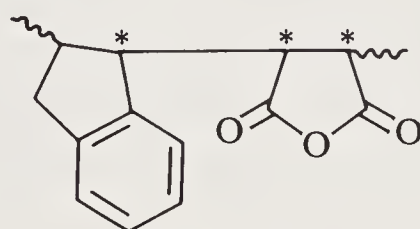
Maleic anhydride has a high dipole moment and phenanthrene exhibits an exceptionally high polarizability. Considering these factors, strong molecular interactions probably exist between this monomer pair due to dipole-induced forces. Heseding and Schneider<sup>(369)</sup> believe this type of interaction brings about the formation of preorientated monomer domains or clusters

which control the copolymerization process. According to this theory, the solvent should play a major role. This conclusion appears to be supported somewhat by the data collected.<sup>(368,369)</sup>

Indene has been copolymerized with MA, under both standard free-radical-initiation conditions<sup>(270,371)</sup> and with free-radical initiation in the presence of lecithin<sup>(372)</sup> to obtain 1:1 copolymer. With the use of benzene or dioxane solvents and BPO initiator at 70°C, copolymers with molecular weight 30–40 thousand were obtained. The alternating indene-co-MA polymer is insoluble in benzene and soluble in dioxane. The non thermoplastic material, with poor film-forming characteristics, starts to decompose at 230°C.<sup>(370)</sup>

The kinetic features and the mechanism of the indene-MA copolymerization have been critically examined.<sup>(371)</sup> Copolymerizations were run at 60°C in a variety of solvents, with BPO initiator. The maximum copolymerization rate occurred at a comonomer feed ratio outside the CTC and copolymer composition, i.e., maximum rate displaced toward an excess of indene in the solvents with strong donor tendency. However, it was concluded from the experimental data that the CTC does participate in the alternating copolymerization process.<sup>(371)</sup>

In the presence of lecithin and using AIBN, copolymers of indene and MA are produced with optical activity.<sup>(372)</sup> The rate of copolymerization and intrinsic viscosities of the copolymers decreased in the presence of the chiral, surface-active (amphiphilic) lecithin. The optical activity observed is presumed to be due to asymmetry induced in the backbone of the copolymer by the chirality of the lecithin. Asymmetry is thought to be induced at the site of the MA moiety.<sup>(372)</sup> Copolymerization is influenced by the electrostatic interaction between MA and the polar hard groups of the lecithin to give **82**, where the \* indicates possible asymmetric centers.



**82**

The copolymer composition, with or without lecithin, is independent of the indene/MA feed ratio and 1:1 alternating. The apparent activation energy, in the presence of lecithin, was 27.3 kcal/mol and about 22.9 kcal/mol without lecithin. The copolymer intrinsic viscosities, as measured in THF at 30°C, varied from 0.34 to 0.62 dl/g, with optical rotation  $[\alpha]_D$  of +0.27 to +4.60.

Copolymerization of MA with *N*-ethyl-2-vinylcarbazole proceeds readily to give equimolar materials.<sup>(374)</sup> For example, AIBN-initiated copolymerization in THF at 50°C gave essentially a quantitative yield of 1:1 copolymer.



Under comparable conditions, *N*-vinylcarbazole and MA gave only approximately 12% yield of polymer which is mainly homopolymer of *N*-vinylcarbazole.<sup>(173,381)</sup> Thus, *N*-ethyl-2-vinylcarbazole and *N*-vinylcarbazole exhibit remarkable differences in both their capability to homopolymerize or copolymerize with MA. To further enlarge the picture, it was recently disclosed that 9-vinylcarbazole will undergo free-radical-initiated copolymerization with dialkyl maleates and fumarates to give good yields of equimolar copolymers.<sup>(1052)</sup>

The copolymerization of acenaphthylene with MA has been studied, by several groups, under a variety of conditions.<sup>(356,375-379,1079)</sup> The two compounds form a eutectic mixture composed of 2 moles of MA and 1 mole of acenaphthalene, and has a melting point of 35.5–36°C. Pure alternating copolymers are best obtained by heating 80:20 (MA:acenaphthylene) molar mixtures of the monomer pair with AIBN or BPO in dioxane. Solid-phase copolymerization with  $\gamma$  rays, using a 1 000-Ci  $^{60}\text{Co}$  source, produces both poly(acenaphthalene) and 1:1 alternating copolymer.<sup>(376-378)</sup> In this case, the maximum rate of copolymerization is observed for the eutectic mixture of the two monomers.<sup>(377,378)</sup> It is considered probable that the solid-state copolymerization of the monomers occurs in a liquid state at the boundary of the two monomer crystals.<sup>(378)</sup> Mixtures of acenaphthylene with MA and with maleimides have been copolymerized on the surface of ethylene-vinyl acetate copolymers, using UV initiation.<sup>(137)</sup> Grafting occurred in both cases.

Free-radical-initiated copolymerization of acenaphthylene-MA mixtures have also been investigated under pressures up to 4 kbars.<sup>(379)</sup> At 60°C, the system showed a low response to pressure, practically independent of the monomer feed compositions. The low response to pressure is not characteristic for all copolymerizations of MA.<sup>(187,382)</sup> The reactivity ratios,  $r_1(\text{acenaphthylene}) = 0.43$  and  $r_2(\text{MA}) = 0.07$ , and the product  $r_1r_2$  of the ratios, 0.03, show the strong tendency toward alternation for copolymerization of this pair. The  $r_1$  value for acenaphthylene is pressure dependent, being 0.32 for 2 920 bars, but the  $r_1r_2$  product remains at 0.03. The results suggest that the cross-propagation reaction dominates over the pressure range studied.<sup>(379)</sup> Similar to stilbene-MA copolymers, alternating copolymers of acenaphthylene-MA exhibit strong excimer fluorescence,<sup>(356)</sup> and this excimer formation has been studied by a time-resolved fluorescence emission spectroscopic (TRES) technique.<sup>(1079)</sup> The equimolar copolymer of 1-vinylnaphthalene-dimethyl fumarate, prepared with AIBN in benzene at 60°C, also exhibits strong excimer and monomer fluorescence.<sup>(400)</sup>

The monomers 1,2-dialin, 1-methyl-3,4-dialin, and dihydroacenaphthene are reported to undergo copolymerization with MA.<sup>(380)</sup> Little is known about the equimolar copolymers. These monomers will not undergo free-radical-initiated homopolymerization nor will the 1,4-dialin monomer undergo copolymerization with MA.



### 10.2.18. Halogenated Monomers

There are mixed opinions on whether vinyl chloride will undergo alternating copolymerization with MA. Equimolar copolymers are claimed when various molar ratios of vinyl chloride and MA are combined and copolymerized in bulk or benzene at 50°C, with AIBN initiator.<sup>(383)</sup> The data showed that highest yields of copolymer occurred at polymerization of equimolar mixtures of the two monomers. Melville and Burnett<sup>(233)</sup> estimate the copolymerization rate constant, at 25°C, is  $1.2 \times 10^4$  liters mol<sup>-1</sup> s<sup>-1</sup>.

From three-component free-radical-initiated polymerization studies of ethylene, vinyl chloride, and MA, it was concluded that MA can undergo alternating copolymerization with vinyl chloride.<sup>(384)</sup> Regardless of the initial monomer composition, a terpolymer was obtained with 50 mol % vinyl chloride and ethylene combined with 50 mol % MA. A CTC has been suggested to play a role in the copolymerization.<sup>(383,384)</sup> However, the fact that the terpolymer contained about 50 mol % MA need not be explained by invoking a CTC mechanism.<sup>(384)</sup>

In a different binary (vinyl chloride–MA) and ternary (vinyl chloride–MA–butadiene) copolymerization study,<sup>(385)</sup> equimolar copolymerization of vinyl chloride and MA does not appear to be a general rule. The formation of equimolar copolymer appears restricted to limited cases, such as very low conversion and sufficiently high MA:vinyl chloride ratios in the monomer feed. It is very hard to see how vinyl chloride, a weak acceptor, could become a donor monomer in the presence of the strong acceptor MA and a CTC formed from the monomer pair regulate copolymerization to obtain 1:1 alternating copolymer. The authors are inclined to agree with Ring's<sup>(385)</sup> evaluation of this monomer pair.

Allyl chloride,<sup>(31,32,34)</sup> propenyl chloride isomers,<sup>(386)</sup> trichloroethylene,<sup>(387)</sup> 1,3-dichloro-2-butene,<sup>(388)</sup> 3-chloro-2-chloromethyl-1-propene,<sup>(389)</sup> and chloroprene<sup>(390)</sup> are all claimed to undergo alternating copolymerization with MA. Isopropenyl chloride is essentially nonpolymerizable by both free-radical and ionic initiators. However, mixtures of isopropenyl chloride and MA in benzene with AIBN, at 60°C, copolymerize quite readily to give colorless materials, with relatively high viscosities.<sup>(386)</sup> The composition of the copolymers were found to be independent of monomer feed ratio and to consist essentially of a 1:1 composition of the monomer pair. In contrast, *cis*- and *trans*-propenyl chloride exhibit low copolymerization rates with MA and the resultant copolymers exhibit much lower specific viscosities than the isopropenyl chloride–co–MA polymers.<sup>(386)</sup>

It is well known that trichloroethylene will not undergo free-radical-initiated polymerization. However, MA and trichloroethylene have been copolymerized with free-radical initiators, both in bulk and solution, to obtain dark-colored materials. Kinetic studies showed the rate of copolymerization

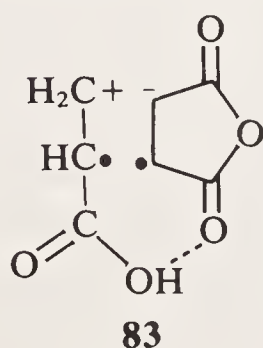
was faster in benzene than acetic anhydride solvent. The monomer reactivity ratios  $r_1 = 3.7 \pm 0.2$  and  $r_2 = 0$  for MA and trichloroethylene,<sup>(387)</sup> respectively, clearly show this should be a nonazeotropic copolymerization system.<sup>(391)</sup>

The monomers 2-chlorobutadiene (chloroprene) and 2,3-dichlorobutadiene, similar to butadiene and isoprene, are also reported to undergo equimolar copolymerization with MA to give materials with a high percentage (>75%) of *cis*-1,4-unsaturation.<sup>(255,390)</sup> The polymerization method employed dioxane solvent and typical free-radical initiators, such as BPO, to give good yields of copolymer.<sup>(225)</sup> The equimolar chloroprene copolymer had a softening temperature of 95–100°C and intrinsic viscosity, measured in DMF (100 ml/g, 25°C) of 0.41 dl/g. The 2,3-dichlorobutadiene copolymer, obtained in a 67% yield, had a softening temperature of 85–90°C.

### 10.2.19. Acrylic and Methacrylic Monomers

With acrylic acid, alternating copolymers are reported to be obtained only when MA is present in excess, otherwise some acrylic acid homopolymer is produced along with the 1:1 copolymer.<sup>(392,737)</sup> These conclusions were reached after various molar ratios of the monomer pair were polymerized both in bulk and solution with BPO initiator.

The reported reactivity ratios for the monomer pair, i.e.,  $r_1(\text{MA}) = 0.007$  and  $r_2(\text{acrylic acid}) = 15.6$  (see Chapter 9), neglecting any CTC formation between the pair, dictate that over the entire range of monomer feed the copolymer composition should be highly enriched with acrylic acid. Since this was not observed, the results were explained by assuming that mixtures of the two monomers form a CTC.<sup>(392)</sup> If in fact only 1:1 alternating copolymer is obtained from equimolar mixtures and/or mixtures with excess MA and after copolymerization occurs the excess MA can be recovered, it is very reasonable to assume the pair forms a CTC. Ultraviolet spectra show new bonds in mixtures of the two monomers at 262, 275 and 286 m $\mu$ , supporting the presence of a CTC. The CTC proposed to account for the copolymerization results has structure **83**. The internal hydrogen bond would be expected to give the **83**-MA CTC much greater stability than only electron or electrostatic interaction experienced by many charge-transfer complexes.





Variation of the comonomer feed, without using excess acrylic acid, did not vary the 1:1 copolymer composition. Thus, the copolymer is believed to be strictly regular or 1:1 alternating.<sup>(392)</sup> When naphthalene is added to the acrylic acid-MA system, the resultant copolymers become enriched with MA.<sup>(392)</sup> Specifically, varying the naphthalene-acrylic acid ratio in the monomer pair-naphthalene feed makes it possible to vary the MA content of the copolymer. It is known that MA and naphthalene form a CTC and the presence of this CTC can significantly affect the course of the MA-styrene copolymerization.<sup>(293,351)</sup> An attempt is also made here to invoke the presence of the MA-naphthalene CTC to account for the observed phenomenon.

The alternating MA-acrylic acid copolymer is a white powder, readily soluble in polar solvents, such as acetone, dioxane, and dimethylsulfoxide and insoluble in aromatic and other nonpolar solvents. The copolymer prepared in the presence of naphthalene exhibits markedly different solubility and other properties, since an increase of MA content in the product beyond 50 mol % disturbs both the regularity and structure of the copolymer.<sup>(392)</sup> The intrinsic viscosity of the alternating copolymer, as measured in dioxane at 25°C, was 1.3 dl/g. In contrast, the copolymers prepared in the presence of naphthalene had intrinsic viscosities of 0.4–0.9 dl/g, depending on the amount of MA in the copolymers. The highest molecular weight ( $\bar{M}_n$ ), for the 1.3 viscosity material, was estimated as  $1.2 \times 10^6$ . The maximum molecular weight of the copolymers prepared in benzene, with an intrinsic viscosity of 0.9 dl/g, was  $0.9 \times 10^6$ . Molecular weights of the copolymers prepared in the presence of naphthalene were of the order  $1.6 \times 10^5$ – $0.8 \times 10^6$ .

Several reports claim that acrylamide and derivatives of acrylamide can undergo alternating copolymerization with MA.<sup>(393,394,1117)</sup> Structural characteristics of the copolymer, prepared in acetone with AIBN at 70°C, were recently investigated to determine distribution of the chemical composition and monomer sequences.<sup>(1122)</sup> The copolymer prepared from *N*-[2(2-methyl-4-oxopentyl)]-acrylamide(diacetone acrylamide), isolated in >70% yield as a fine white powder, analyzed correctly for an equimolar copolymer.<sup>(394)</sup> Acryloyl-substituted azepine is also reported to undergo copolymerization with MA to give 1:1 copolymer.<sup>(395)</sup>

Several reports have issued claiming alternating copolymers of methacrylate monomers with MA.<sup>(396–399)</sup> Low-molecular-weight alternating copolymers of methyl methacrylate-MA are obtained from copolymerization of the monomer pair in ethyl acetate with AIBN initiator.<sup>(396)</sup> Tsang<sup>(16)</sup> also showed that methyl acrylate and methyl methacrylate have a tendency to undergo equimolar copolymerization with MA. It is doubtful these are truly alternating copolymers, since other studies have shown that alkyl acrylates and methacrylates have a great tendency not to copolymerize in a 1:1 fashion with MA (see Sec. 9.2.6). Unperturbed molecular dimensions, steric parameters, and repeating unit structure were discussed. Case and Loucheux<sup>(397)</sup> claim that



copolymerization in benzene involves a CTC between the two monomers, tending to alternating copolymers. Bulk copolymerization follows terminal model kinetics to produce a random copolymer (see Chapter 9).<sup>(397)</sup>

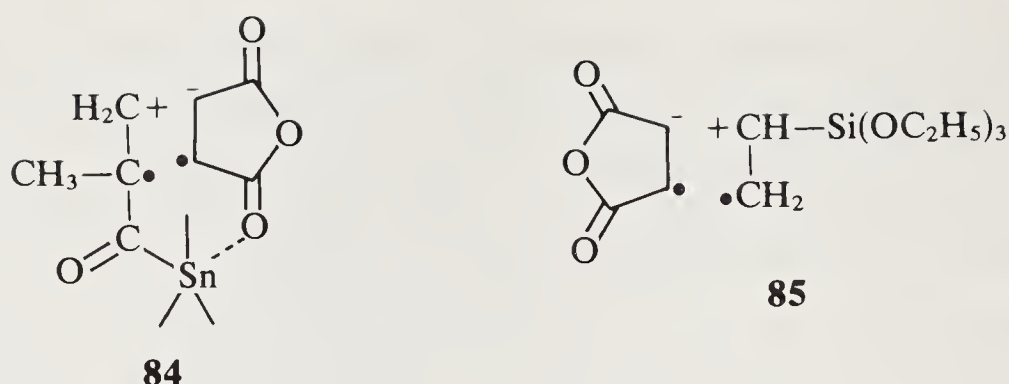
Monomers such as methacryloyl-*l*-valine and *d*-valine methyl esters have been photopolymerized with MA in dioxane at 35°C.<sup>(398,399)</sup> Low-molecular-weight materials, 4 300–12,000, having an equimolar ratio of the two monomers were obtained regardless of the starting monomer feed and polymerization time. Copolymerization rates were slower in ethyl acetate and copolymer was not produced in several other solvents. The polymerization rate and molecular weight increased with an increasing MA feed. Circular dichroism studies showed the introduction of asymmetric centers along the backbone of the polymer main chain. The results showed a remarkable case had been discovered where both alternating and stereoregular copolymerization had occurred for a monomer pair.

Optically active copolymers of (–)-1-phenylethyl methacrylate and MA have also been prepared.<sup>(401)</sup> The copolymer remained optically active even after removal of the optically active ester group pendent on the polymer backbone. The copolymers were not strictly 1:1 alternating materials, such as the (–)-1-phenylethyl vinyl ether–MA copolymers.<sup>(80)</sup> The work on these optically active copolymers is an excellent demonstration of the importance of steric effects in determining the configuration of a newly formed repeating unit on a polymer backbone.

#### 10.2.20. Organometallic Monomers

Several tin,<sup>(104)</sup> silicone,<sup>(104,402–405)</sup> and iron<sup>(410,411)</sup> containing compounds with vinyl or acrylic residues, have been shown to copolymerize with MA. Tributyltin methacrylate is reported to copolymerize readily with MA to give equimolar copolymer.<sup>(104,402,1074)</sup> Reactivity ratios for the copolymerization are reported in the table in the appendix to Chapter 9. Copolymer, with a softening temperature of 120–125°C, can be prepared in >86% yield by heating equimolar mixtures of the monomer pair and BPO at 60°C. Elemental data from several copolymerizations show that equimolar materials are obtained regardless of monomer feed ratios. It is suggested that the MA–tributyltin methacrylate pair forms a CTC with internal coordination bonds **84**, similar to the described MA–acrylic acid system, and this CTC **84** accounts for alternating copolymerization control.

Vinyltriethoxysilane forms a yellow-colored solution when combined with MA.<sup>(104,402–405)</sup> These yellow mixtures in the presence of free-radical initiators form hard, brittle resins, soluble in ether, dioxane, benzene, and toluene, with molecular weights up to approximately 3 000.<sup>(402)</sup> Ultraviolet absorption maxima for chloroform mixtures of the pair give support for a CTC **85**. On the basis of the equilibrium constant (see table in the appendix to this chapter)



for the CTC, 0.30–0.384 liter/mol, a CTC mechanism was invoked to explain the formation of alternating copolymer. However, the reactivity ratios  $r_1 = 0.035$  and  $r_2(\text{vinyltriethoxysilane}) = 0.004$  and reactivity ratio product  $r_1 r_2 = 1.4 \times 10^{-4}$  (see Chapter 9) clearly show that a strong alternating tendency should exist for this monomer pair.

Alternating vinyl trimethylsilyl ether–MA and vinyl trimethylsilyl ether–maleimide copolymers are readily prepared by heating mixtures of the two monomer pairs in the presence of free-radical initiators.<sup>(404)</sup> Equimolar MA copolymers were prepared with intrinsic viscosities as high as 1.68 dl/g, measured in acetone at 25°C, and with a softening temperature of approximately 206°C. The equimolar maleimide copolymer, with an intrinsic viscosity of 0.50 dl/g, had a softening temperature of approximately 261°C. Similar to the vinyl ethers, vinyl trimethylsilyl ether is normally highly resistant to free-radical polymerization.

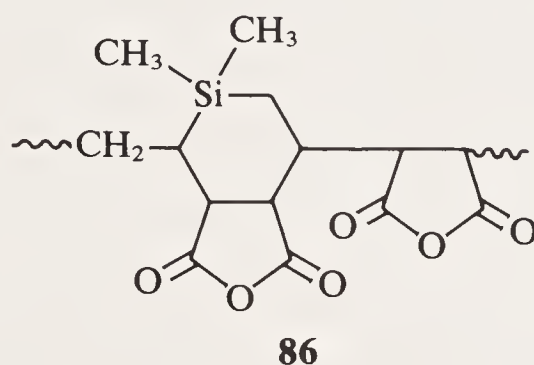
Vinyl silanes, such as trimethylvinylsilane and dimethyldivinylsilane, were reported by Kanazashi<sup>(406)</sup> to be resistant to free-radical-initiated polymerization. However, trimethylvinylsilane was later shown to copolymerize with several other vinyl monomers.<sup>(407)</sup> Butler and Campus<sup>(126)</sup> showed that Kanazashi's<sup>(406)</sup> paper was incorrect concerning dimethyldivinylsilane, i.e., it will undergo free-radical-initiated homopolymerization to give soluble resins. Additional studies have shown that both vinylsilanes as well as divinylcyclopentamethylenesilane will copolymerize with MA, in the presence of free-radical initiators.<sup>(126)</sup> Trimethylvinylsilane forms a 1:1 alternating material, while dimethyldivinylsilane and divinylcyclopentamethylenesilane, being 1,4-pentadienes, form 1:2 cyclopolymers (Sec. 10.2). For the study, a wide range of monomer feed ratios were combined with 1% by weight AIBN, benzene solvent, and heated at 60°C. The trimethylvinylsilane copolymers had intrinsic viscosities, measured in acetone at 25°C, of 0.06–0.08 dl/g. The dimethyldivinylsilane copolymers, evaluated under the same conditions, had slightly higher molecular weights, with inherent viscosities in the range of 0.07–0.13 dl/g.

Over a relatively wide range of initial monomer compositions, the molar fraction of MA in the trimethylvinylsilane copolymer remains constant and equal to 1:1, except for very dilute solutions in vinylsilane where a value of 0.547 was found. The rate of copolymerization was greatest at equimolar



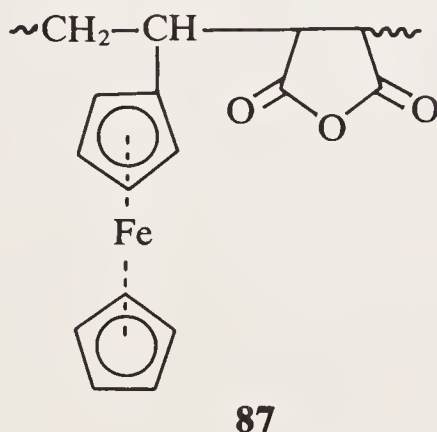
feed ratios. A composition average for nine runs showed 13.96% Si, with theory for a 1:1 copolymer being 14.15% Si.

Using a wide range of monomer feed ratios, the molar fraction of MA in the dimethyldivinylsilane copolymers was equal to a 2:1 ratio. The maximum rate of copolymerization was observed for a 2:1 molar excess of MA. In contrast to the trimethylvinylsilane copolymers, the dimethyldivinylsilane copolymers precipitated as formed from benzene. However, isolated polymer was soluble in polar solvents. The absence of double bonds, based on IR and NMR studies, solubility, a proven 1:2 dimethyldivinylsilane:MA copolymer composition, and an average silicone content of 9.17% (theory, 9.11% for a 1:2 material) support structure **86**. The structure is envisioned as developing by a bimolecular alternating inter-intramolecular copolymerization mechanism.<sup>(126)</sup>



Vinylferrocene is one of the few transition-metal-containing monomers that will both homopolymerize and copolymerize with other vinyl monomers in the presence of free-radical initiators.<sup>(408-411)</sup>

Copolymerization of vinylferrocene with MA, using AIBN in benzene-ethyl acetate solvent mixture at 70°C, is relatively slow, especially when the molar amount of MA in the feed exceeds 50%.<sup>(411)</sup> Polymerization does not occur when the mol % of MA exceeds 70. The product of the reactivity ratios,  $r_1 r_2 = 0.0042$ , clearly shows a strong tendency to alternation. Composition, gel permeation chromatography, and IR and NMR analyses showed the copolymers approached 1:1 at feeds in excess of 46 mol % vinylferrocene. Structure **87** represents the alternating vinylferrocene-MA copolymer. Tributylborane has also been evaluated as a catalyst to prepare the copolymer.<sup>(410)</sup>



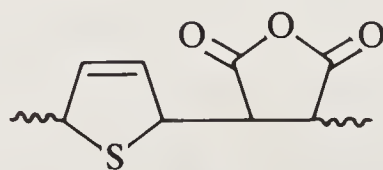


### 10.2.21. Sulfur Containing Monomers

Ethyl, isobutyl, and phenyl vinyl sulfide behave as typical good electron-donating monomers, readily undergoing alternative copolymerization with a strong electron acceptor such as MA.<sup>(264,265,412,413)</sup> Vinyl sulfide-MA mixtures turn yellow soon after mixing and undergo copolymerization at moderate temperatures, even in the absence of free-radical initiators. Spectroscopic evidence shows the equilibrium constants for the vinyl sulfide-MA charge-transfer complexes are quite small (see table in appendix to this chapter). Ethyl vinyl sulfide-MA mixtures undergo spontaneous copolymerization at a faster rate than ethyl vinyl ether-MA mixtures. This is hard to understand since the equilibrium constants (table in appendix to this chapter) for the two charge-transfer complexes are comparable. Vinyl sulfide-MA systems show maximum copolymerization rates and reduced viscosities for 1:1 monomer mixtures (benzene, AIBN, 60°C).<sup>(412)</sup> Also, over a wide range of monomer feed ratios, equimolar copolymers were obtained. At 1:1 feed ratios the reduced viscosities, measured in DMF at 30°C, for the phenyl vinyl sulfide and ethyl vinyl sulfide copolymers were, respectively, 0.61 and 2.54 dl/g.

Plots of time versus conversion for the copolymerization of 1:1 mixtures of phenyl vinyl sulfide with MA at 40, 50, and 60°C were linear plots. Fitting the results to a straight line using the Arrhenius equation gave an apparent overall activation energy of 22.4 kcal/mole,<sup>(412)</sup> in good agreement with 22.0 kcal/mol reported for the *p*-dioxene-MA pair<sup>(414)</sup> and 23 kcal/mol reported for the dodecyl vinyl ether-MA copolymer.<sup>(100)</sup> Biosynthetic asymmetric oxidation of the phenylvinyl sulfide-co-MA polymers produces optically active materials.<sup>(413)</sup>

Similar to furan and benzofuran monomers,<sup>(116,117)</sup> thiophene and 1-benzothiophene<sup>(116,415)</sup> are also known to copolymerize in a 1:1 fashion with MA. Thiophene will not undergo free-radical homopolymerization or copolymerization with monomers such as styrene, methyl methacrylate, or acrylonitrile. However, when an equimolar mixture of thiophene and MA are combined with chloroform containing AIBN and heated at 60°C, a white copolymer starts to precipitate after only a few minutes reaction time. Varying the molar feed ratios showed that both yields and reduced viscosities were maximum for equimolar feeds. Copolymerizations in solution from 1 bar to 3 kbars show that rates and yields are increased with pressure.<sup>(187)</sup> Through composition studies and comparing the NMR spectrum of the copolymer with the NMR spectra of 2,3- and 2,5-dihydrothiophene, structure **88** was assigned to the copolymer.



**88**

By analogy with furan-MA copolymerizations,<sup>(108)</sup> propagation is believed to occur by the thiophene-MA CTC,<sup>(415)</sup> which has an equilibrium constant (table in appendix to this chapter) of only 0.02 liter/mole.<sup>(416)</sup> The overall activation energy for the copolymerization was estimated as 17.0 kcal/mol. Radiation-initiated (<sup>60</sup>Co  $\gamma$  rays) copolymerization of thiophene with MA has also been studied.<sup>(417)</sup> Copolymerization proceeds via a free-radical mechanism with bimolecular termination of propagating polymer radicals. An apparent activation energy of 5.3 kcal/mol was estimated. The copolymerizations went best in halogenated solvents with the highest rates observed at equimolar feed compositions. Nuclear magnetic resonance studies showed the alternating copolymer also had structure **88**.

Under the influence of AIBN, benzothiophene and indole also form alternating copolymer with MA.<sup>(116)</sup> Varying the molar feed ratios, it was found that both yields and molecular weights were highest for equimolar feeds. For the benzothiophene-MA system, copolymers were prepared with reduced viscosities, measured in acetone (0.5 g/100 ml at 25°C), of 0.09–0.16 dl/g. In comparison, the reduced viscosities of the indole-MA copolymers, measured in dimethylsulfoxide (0.5 g/100 ml at 25°C) were only 0.07–0.09 dl/g. Copolymer compositions clearly showed that only equimolar materials were obtained in all cases.

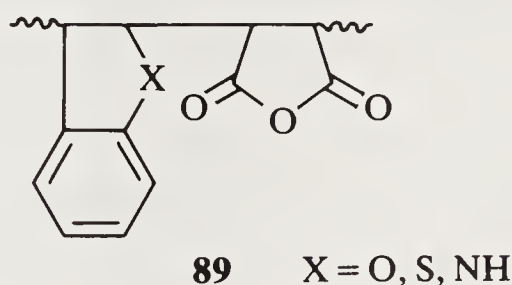
Several vinyl, propenyl, and isopropenyl substituted thiophenes, with halogen substituents, have also been mixed with MA and copolymerized,<sup>(118)</sup> using peroxides at 65–70°C. The structures of the various copolymers were not reported. However, use of equimolar feeds would suggest that some of the copolymers could be of the alternating type. Copolymerization of 4-methyl-5-vinylthiazole-MA mixtures was also studied.<sup>(118)</sup> Alternating copolymers were also probably formed from this comonomer pair.

The equilibrium constants for the charge-transfer complexes of MA with benzofuran (BF), benzothiophene (BT), and indole (table in appendix to this chapter) follow the order MA-BT > MA-indole » MA-BF. This suggests that the copolymerization rates should follow the same order. This is not the case; time-conversion curves show copolymerization rates of the three monomer pairs to be MA-BF > MA-BT > MA-indole. The same sequence was also found for maximum conversions at “infinite” time.<sup>(116)</sup> The results suggest clearly that the reactivity of the comonomers to form copolymers with MA is predominately governed by resonance stabilization of the various monomer pairs. However, Goethals *et al.*<sup>(116)</sup> suggest that the copolymerization of MA with benzothiophene or indole, to give structure **89**, may still occur by the charge-transfer complexes making the copolymerizations thermodynamically possible.

Very recently, the copolymerization of 2-(vinylthio)benzothiazole<sup>(418)</sup> and *p*-oxathiene<sup>(419)</sup> with MA were investigated. Only the *p*-oxathiene copolymer appeared to have the 1:1 alternating structure. The results would be



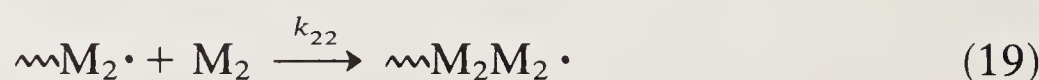
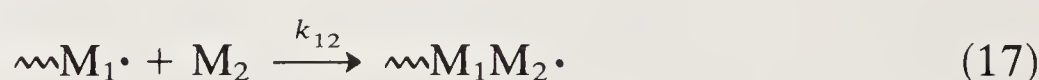
expected since the 2-(vinylthio)benzothiazol homopolymerizes readily with free-radical initiators, with a 20.9-kcal/mol activation energy. The results of the *p*-oxathiene work support the thought that alternating copolymerizations of two monomers is related more closely to the donating power of the electron donor than to a resonance or polarity property of the donor monomer.



The photocooligomerization of 1,3-dithiolane with MA has recently been explored by Ouchi and Aso.<sup>(1022)</sup> Mixtures of the two monomers formed a yellow solution ( $\lambda_{\max} = 430$  nm) that turned orange ( $\lambda_{\max} = 450$  nm) on photoirradiation. The authors<sup>(1022)</sup> suggest that the dithiolane–MA CTC takes part in the cooligomerization reaction. Rates of polymerization and molecular weights were greatest at 1 : 1 feeds.

### 10.3. COPOLYMERIZATION MECHANISM

When two types of vinyl monomers  $M_1$  and  $M_2$  are combined for polymerization, random copolymers are generally formed via four elementary reactions, Eqs. (16)–(19).



For the many alternating copolymer systems briefly discussed in this chapter, MA ( $M_1$ ) is adjacent to some comonomer  $M_2$ , and  $M_2$  is adjacent to  $M_1$ . The respective  $M_1 M_1$  and  $M_2 M_2$  segments, resulting from Eqs. (16) and (19), are essentially nonexistent. Only the cross-propagation reactions, Eqs. (17) and (18), are observed. This very special copolymerization reaction occurs readily between the strong electron-acceptor MA and many different types of electron-donor monomers.



For conventional free-radical copolymerizations, polar effects of growing polymer radicals on the approaching monomer is expressed by the Alfrey–Price<sup>(1)</sup>  $Q - e$  scheme, where the copolymerization tendency, i.e., product of monomer reactivity ratios, may be expressed, Eq. (20), in terms of  $e$  values.

$$r_1 r_2 = \exp [-(e_1 - e_2)^2] \quad (20)$$

As shown in Eq. (20), the copolymerization tendency increases with an increase in the  $e$  value of the two monomers. Therefore, an essentially alternating copolymer is predicted above a certain value, i.e., the larger the absolute value between  $e_2$  and  $e_1$  becomes, the greater the tendency for alternation becomes. Since MA has  $e = 2.25$  and most of the monomers discussed have fairly large negative  $e$  values, alternating copolymers were predictable for many of the MA comonomer pairs discussed.

Toda *et al.*<sup>(420)</sup> suggested the use of the alternating diad,  $F_{12}$  and  $F_{21}$ , as the measure of alternating degree instead of  $r_1 r_2$ , where  $F_{12} + F_{21}$  is given by Eq. (21).

$$F_{12} + F_{21} = 2/(2 + r_1 u + r_2 u) \quad (21)$$

where  $u$  is the monomer feed ratio,  $[M_1]/[M_2]$ .

Combining the two Alfrey–Price<sup>(1)</sup> reactivity ratio equations [(22) and (23)] with Eq. (21) gives Eq. (24) as a full expression of this concept.

$$r_1 = (Q_1/Q_2) \exp [-e_1(e_1 - e_2)] \quad (22)$$

$$r_2 = (Q_2/Q_1) \exp [-e_2(e_2 - e_1)] \quad (23)$$

$$F_{12} + F_{21} = 2/\{2 + (Q_1/Q_2) \exp [-e_1(e_1 - e_2)]u + (Q_2/Q_1) \exp [-e_2(e_2 - e_1)]/u\} \quad (24)$$

When  $Q_1$  is equal to  $Q_2$ , Eq. (21) attains a maximum. Kawabata *et al.*<sup>(421)</sup> developed a  $Q$ - $e$  map for two series. The series consisting of 1,3-dienes and styrene, would be the most favored for alternating copolymerization with MA, because the difference in the  $e$  values is relatively large as compared with the difference in  $Q$  values.<sup>(422)</sup> Using MA, methyl methacrylates, and acrylonitrile mixtures, other methods have also been explored for evaluating the alternating tendency in copolymerization.<sup>(423)</sup>

Since about mid-1946, essentially three controversial theories for free-radical-initiated alternating copolymerizations have come to exist. One theory called terminal or “free” monomer mechanism, which follows from the Alfrey–Price<sup>(1)</sup>  $Q$ - $e$  concepts, holds that electrostatic interaction between the propagating radical and the monomer molecule brings about the cross-propagation reaction.<sup>(1,14,30)</sup> Walling *et al.*<sup>(13,17)</sup> modified this mechanism by suggesting that the stabilization of the transition states for the two cross propagations was due to the formation of charge-transfer complexes, but not due to the

electrostatic interactions proposed by Price.<sup>(1,14)</sup> Conventional free-radical kinetics were claimed for all cases.<sup>(13,25,27,424,425)</sup> The third concept, growing out of the work by Bartlett and Nozaki,<sup>(4)</sup> holds that monomer–monomer interactions (charge-transfer complexes) play a significant or decisive role in the copolymerizations.<sup>(5–9,11,12,94,426,456,466,473)</sup> This concept favors electron-donor–electron-acceptor interactions, i.e., a partial electron transfer in the form of a transition state at the time of the growth step. A recent variation of these mechanisms calls for simultaneous participation of both “free” monomers and charge-transfer complexes in the copolymerization reaction.<sup>(20,88,427–429,558,1037)</sup>

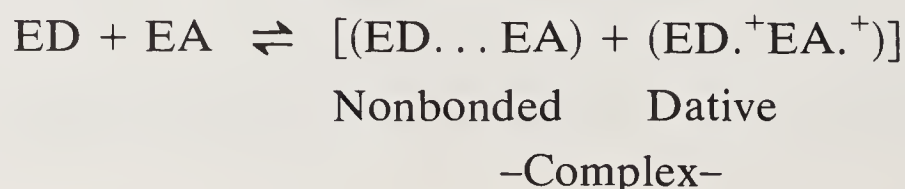
A large number of studies have been devoted to alternating copolymerizations, with most of the effort centered about MA. In many cases, these studies have attempted to explain the observed general characteristics of alternating copolymerization, which includes the following:

1. Some of the monomer mixtures, in the absence of free-radical initiators, will undergo thermal or spontaneous copolymerization.
2. Over a wide range of monomer feed ratios, the copolymers have 1 : 1 alternating structures.
3. Charge-transfer complexes, confirmed by spectroscopy, exist in the reaction medium.
4. The reaction rates are usually maximum at equimolar feeds and show substantial dependence on solvents and other additives.
5. The copolymerizations may be initiated photochemically.
6. Inhibition of the allyl-degradative type chain-transfer reaction can occur.
7. Polymerizations may stop as soon as either one of the monomers is consumed in the copolymerization.

A full discussion of all the above features and possible mechanisms for alternating copolymerizations is beyond the scope of this book. However, an attempt is made to give a brief survey of the subject, confining coverage mainly to MA systems and absence of “activators,” e.g., metal halides and organometallic halides. Those interested in a full discussion of charge-transfer complexes and alternating copolymerization are advised to consult the many books and reviews on the subject.<sup>(28,241,429–447,449,450,489,1058)</sup>

### 10.3.1. Charge-Transfer Complexes

In solution, when a ground-state CTC is formed between an electron donor (ED) and an electron acceptor (EA) an equilibrium reaction occurs:





with a wave-function expression existing for the CTC showing linear combination of wave functions of the nonbonded state and the bonded state:

$$\psi_{\text{CTC}} = a\psi(\text{ED} \dots \text{EA}) + b\psi(\text{ED}^+ \text{EA}^-)$$

where  $a \gg b$  in the ground state and  $b \gg a$  in the excited state.

The constant  $K$  for this equilibrium is expressed in its simplified form as follows:

$$K = \frac{[\text{CTC}]}{[\text{ED}][\text{EA}]}$$

where  $[\text{CTC}]$ ,  $[\text{ED}]$ , and  $[\text{EA}]$  are the concentrations of the respective species.

The formation of the charge-transfer complexes considered to be of the  $\pi$ -donor- $\pi$ -acceptor type for most of the system discussed<sup>(150,182,441,466)</sup> and their equilibrium concentrations are not only influenced by the donor and acceptor strength of the respective molecule but also by resonance stabilization, steric effects, van der Waals forces, and hydrogen bonding.<sup>(149,150,392,452,462)</sup> Aromatic solvents are also considered  $\pi$  donors.<sup>(10,455,466,472)</sup> Solvents such as ketones, alcohols, ethers, amines and amides, and monomers with these residues act as  $n$ -donors, since the electron which participates in the CTC does not come from an electron pair which is part of a bond, but instead comes from a free-electron pair.<sup>(182,466)</sup> The CTC stabilities are also influenced by temperature, the presence of "activators," and donor solvents.

As shown in this chapter, this book covers only the systems where the EA is MA. However, ED represents a wide variety of vinyl ethers, olefins, styrenes, allyl monomers, etc., and many nonpolymerizable additives.

While attempting to establish the existence and role of the CTC in alternating copolymerizations, many authors have determined the equilibrium constant ( $K$ ) for a large number of MA-comonomer pairs (table in appendix to this chapter). Other charge-transfer complexes of MA have also been extensively investigated,<sup>(453-456)</sup> by the use of ultraviolet<sup>(457-459)</sup> and NMR<sup>(460-462)</sup> spectroscopic methods (table in appendix to this chapter). Identification of the CTC is centered on the concentration and temperature dependence of the absorption in the visible and ultraviolet spectra. In NMR, the acceptor or donor protons undergo a chemical shift when the CTC is formed and this variation is used to determine the  $K$  values. Calorimetric methods have also been used to determine equilibrium constants.<sup>(149,1059)</sup> Caze and Loucheux<sup>(151)</sup> provide a good discussion of how solvents cause variations of  $K$  values for donor-acceptor pairs. The continuous variations procedure, developed by Job<sup>(463)</sup> and Vosberg and Cooper<sup>(464)</sup> is usually used to determine CTC stoichiometry. Equilibrium constants are generally quite small (table in appendix to this chapter), showing that CTC concentration is considerably below that of the free monomers.



10.4. BINARY COPOLYMERIZATIONS

Since Bartlett and Nozaki<sup>(4)</sup> originated the concept that a CTC could play an important role in alternating copolymerizations, numerous studies have been conducted to substantiate this concept. Iwatsuki and coworkers,<sup>(54,55,95,96,98,465,466)</sup> from their many studies on vinyl ether–MA copolymerizations, suggested that the reactivity of the CTC increases with the equilibrium constant for the CTC formation and make a tentative classification of charge-transfer polymerizations (Table 10.13).

The work of several authors tends to support the concept that the magnitude of the equilibrium constant ( $K$ ) for the CTC can be considered as a measure of alternating copolymerizability.<sup>(54,65,70,203,466)</sup> Kokubo *et al.*<sup>(466)</sup> found that the mean rates of spontaneous copolymerization (%/min) for 1,2-dimethoxyethylene, 2-chloroethyl vinyl ether, and *p*-dioxene with MA, under comparable conditions, were 0.092, 0.089, and 0.006, respectively. This agrees with the order of the  $K$  values for these three charge-transfer complexes (see table in Appendix to this chapter).

Hallensleben's<sup>(70)</sup> work with *n*-butyl (NBVE), isobutyl (IBVE), and *tert*-butyl vinyl ether (TBVE) copolymerization with MA shows the same effect. The copolymerization rates follow the order TBVE>IBVE > NVBE, with corresponding  $K$  values (table in appendix to this chapter) of 2.12, 1.11, and 0.56 liter mole<sup>-1</sup>.

Table 10.13. Classification of Charge-Transfer Copolymerizations<sup>a</sup>

$K$	Class	Example	Behavior
0.01	A	<i>p</i> -Dioxene–MA	Random copolymerization
	B		Alternating copolymerization with free-radical initiators
0.10	C	Chloroethyl vinyl ether–MA	Spontaneous alternating copolymerization near room temperature ( $K$ decreases with solvent polarity)
1.0	D	Dimethoxyethylene–MA	Spontaneous ionic polymerization ( $K$ increases with solvent polarity)
5.0		<i>N</i> -Vinylcarbazole- <i>p</i> -chloranil	
∞	E	4-Vinylpyridine- <i>p</i> -chloranil	Formation of separable, stable charge-transfer complexes that cannot initiate polymerization

<sup>a</sup> Reprinted with permission from *Macromolecules* **1** (6), 482 (1968). Copyright © 1968, American Chemical Society. Also see References 51, 467, and 468.

Fujimori<sup>(65)</sup> showed that the above concept also holds for ethyl vinyl ether (EVE), 2,3-dihydropyran (DHP), and divinyl ether (DVE). The  $e$  values of DHP, EVE, and DVE (Table 10.14), respectively, become negatively larger as the equilibrium constants of their CTC with MA increase in the same order:  $K(\text{DHP-MA}) = 0.11$ ;  $K(\text{EVE-MA}) = 0.15$ , and  $K(\text{DVE-MA}) = 0.18 \text{ liter mole}^{-1}$ . Under the same conditions, the conversion for the copolymerization of DHP with MA after 10 h was comparable to that of the copolymerization of EVE with MA after only 100 min. It is hard to conceive how such a small difference between the  $K$  values of DHP and EVE with MA could bring about such a great difference between the copolymerization rates of the two pairs. Zeegers and Butler<sup>(521)</sup> claimed that the polymerization kinetics of DVE with MA could be explained without the intervention of a CTC, but charge-transfer complexes may participate in competing reactions.

Inaki *et al.*<sup>(90)</sup> demonstrated that the rates of copolymerization of *cis* (I) and *trans*-methyl propenyl (II) ethers and 2,3-dihydropyran (III) with MA follows the order  $\text{I} > \text{II} > \text{III}$ . This order agrees with the order of the equilibrium constants reported for these three pairs (see Chapter 10 Appendix).

Copolymerization rates of vinylcyclohexane and  $\alpha$ -methylvinylcyclohexane with MA also reflect the donor ability of the two olefins.<sup>(203)</sup> Vinylcyclohexane and  $\alpha$ -methylvinylcyclohexane with  $K$  values of 2.21 and 2.44 liter mole<sup>-1</sup> (Chapter 10 Appendix) show reaction rates, respectively, of  $0.3 \times 10^{-5}$  and  $1.5 \times 10^{-5} \text{ mole liter}^{-1} \text{ s}^{-1}$ .

Nimoura and Susuki,<sup>(469)</sup> on the basis of the results obtained from the copolymerizations of a few  $\alpha,\beta$ -distributed olefins, observed a relationship between the Alfrey-Price<sup>(1)</sup>  $e$  values of the monomers and the formation of the CTC. They postulated that when the difference in the  $e$  values<sup>(41)</sup> between an electron donor and electron acceptor is greater than 3, a CTC such as that formed between *p*-dioxene-MA<sup>(414)</sup> is observed, but not when the difference is  $<3$ . Alternating copolymers are formed when the difference is as low as 2.5. However, below 2.5 only random copolymers are obtained. Additionally, they suggest the mechanism changes from the CTC mechanism of Walling

Table 10.14. Alfrey-Price  $Q$  and  $e$  Values of Vinyl Ethers and Equilibrium Constants of these Ethers with MA<sup>a</sup>

Monomer	2,3-Dihydro-PYRAN	Ethyl vinyl ether	<i>n</i> -Butyl vinyl ether	Divinyl ether	<i>t</i> -Butyl vinyl ether
$e$	-0.93	-1.12	-1.20	-1.28	-1.58
$Q$	-0.013	0.032	0.087	0.037	0.15
$K$ (liter/mole) <sup>a</sup>	0.11	0.15	—	0.18	2.12

<sup>a</sup> Determined in *n*-heptane at 24°C.



*et al.*<sup>(17)</sup> to the mechanism of Iwatsuki *et al.*<sup>(414)</sup> in the sequence in which the difference between the  $e$  values increases beyond 2.5.

Exceptions to the type of trends observed in Table 10.14 have been observed.<sup>(116,412)</sup> The equilibrium constants for benzofuran, indole, and benzothiophene with MA (table in appendix to this chapter) follow the order 0.01, 0.28, and 0.30 liter mole<sup>-1</sup>. The actual rates of copolymerizations of these three monomers with MA follow the order benzofuran > benzothiophene > indole. If the only factor determining the copolymerizability of these three monomers with MA had been the values of the equilibrium constants, the order of decreasing rates should have been benzothiophene > indole > benzofuran. Since this is not the case, Goethals *et al.*<sup>(116)</sup> conclude that the formation of the CTC need not be the most important factor in determining the reactivity of these copolymerizations. For these three pairs, it appears that the reactivity of these compounds to form copolymers with MA is determined by two factors: CTC formation and loss of stabilization energy.<sup>(116)</sup> The high copolymerizability of the benzofuran-MA pair may possibly be due to activation of the CTC by the low stabilization energy of the furan ring. Polymerization is of the classical Alfrey-Price<sup>(1)</sup> type and the perfect alternating structure of the copolymers is due to the impossibility of homopolymerization. The same line of reasoning might also be applied to stilbene,<sup>(354,355)</sup> acenaphthylene,<sup>(376-379)</sup> phenanthrene,<sup>(367)</sup> and indene<sup>(369)</sup> copolymerizations with MA.

Otsu and Inoue<sup>(412)</sup> reported that phenyl vinyl sulfide (PVS) and ethyl vinyl sulfide (EVS) also fail to agree with the trend in Table 10.14. It was found that EVS and PVS copolymerization rates with MA follows the pattern EVS  $\gg$  PVS. The Alfrey-Price<sup>(1)</sup>  $e$  values for PVS and EVS are -1.40 and -0.12, respectively,<sup>(41)</sup> with the corresponding equilibrium constants (table in appendix to this chapter) of 0.090 and 0.035 liter mole<sup>-1</sup>. Thus, PVS should copolymerize much faster with MA than EVS. This shows the Nimoura and Susuki<sup>(469)</sup> concept does not hold in all cases.

The equilibrium constant for the difluoromaleic anhydride-styrene complex (0.89 liter mole<sup>-1</sup>) is much larger than the MA-styrene constant (0.33 liter mole<sup>-1</sup>) determined under the same conditions.<sup>(1051)</sup> The same holds true for the difluoromaleic anhydride-phenyl vinyl ether (0.95 liter mole<sup>-1</sup>) and MA-phenyl vinyl ether (0.16 liter mole<sup>-1</sup>) pairs. However, no relationship was found between the numerical value of the equilibrium constants and the tendency of alternating copolymerization initiated by free-radical initiators. Regel and Canessa<sup>(1051)</sup> believe that symmetry considerations lead to the conclusion that CTC's have no significant involvement in these copolymerization. Their kinetic results for the phenyl vinyl ether-difluoromaleic anhydride system supports this statement, showing that the formation of the CTC is not the rate-determining step of copolymerization. This is further evidence that the Nimoura and Susuki<sup>(469)</sup> concept has limited applicability.



According to Frank,<sup>(184)</sup> the alternating tendency for olefin-MA copolymerizations should be based on the donor effect of the olefin and acceptor effect of the anhydride, covered by the electrostatic relationship given in the *Q-e* diagram. Thus, ethylene with *e* = -0.43 and MA with *e* = 2.25 should readily undergo alternating copolymerization.<sup>(41)</sup>

As shown in the table in the appendix to this chapter, thiophene and MA form a CTC with an equilibrium constant of 0.02 liter mole<sup>-1</sup>. Cardon and Goethals<sup>(415)</sup> point out that thiophene must experience a loss of about 29 kcal/mol of resonance energy in order to copolymerize with MA. They suggest that copolymerization of this pair must occur via a concerted propagation step, not free monomers, to account for overcoming the loss of the resonance-energy obstacle.

It should be noted (table in appendix to this chapter) that several systems show that the equilibrium constants often decrease with an increase of solvent polarity (see Chapter 4), since in polar solvents free monomer is better stabilized than the CTC. In alternating copolymerizations, the solvent-monomer interactions usually play a major role,<sup>(21,55,65-68,98,151,203,295,371,392,416,432,464,470-475,625,1059,1062)</sup> since many solvents can also form charge-transfer

Table 10.15. Solvent-MA CTC Equilibrium Constants (*K*)

Solvent	Temperature (°C)	<i>K</i> (liter mole <sup>-1</sup> )	Reference
Methyl ethyl ketone	60	0.62	314
Chloroform	60	0.14	314
	25	0	151
Cyclohexane	36	0.01	21
Dimethylsulfoxide	60	1.32	314
Benzene	25	0.68	470
	25	0.15	20, 21
	25	0.09	416
	39.5	2.13	1059
Toluene	25	0.40	10
	25	0.60	470
Acetone	25	0.667	21
	25	0.75	151
	25	0.79	314
	39.5	1.37	1059
<i>N,N</i> -Dimethylaniline	60	1.50	470
<i>N,N</i> -Dimethylformamide	25	0.034	67
<i>N,N</i> -Dimethylacetamide	25	0.027	67
<i>N</i> -Methylpyrrolidone	25	0.028	67
	25	0.015	416
Tetrahydrofuran	36	0.086	475
	25	0.44	21
	24	0.086	100, 474
	28	0.48	1062

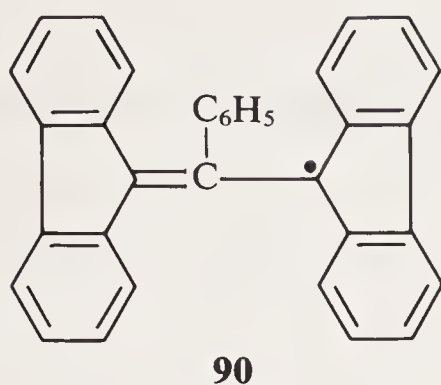
complexes with MA of the same magnitude or larger than many of the monomers discussed in this chapter (Table 10.15). For example, a general decrease in rates of copolymerization of 2,3-dihydropyran,<sup>(65)</sup> *n*-butyl vinyl ether,<sup>(68)</sup> and divinyl ether<sup>(474)</sup> with MA is observed with increasing dielectric strength of solvents.<sup>(475)</sup> For the styrene-MA pair, the activation energy interestingly drops from 18.8 kcal/mol in dichloroethane to 13.8 kcal/mol in acetone, showing how solvent changes can significantly affect the initiation reaction. Solvents can also play a role in conventional free-radical-initiated homo and copolymerizations, acting as a reagent in some cases to significantly affect the elementary reactions, initiation, propagation, termination, and chain-transfer processes.<sup>(530,1042,1054)</sup>

When *N,N*-dimethylaniline (DMA) or naphthalene is added to styrene-MA systems, the incorporation of MA in the copolymers is increased and the rate of copolymerization decreases.<sup>(293-297,471)</sup> The rate drop is attributed to increased degradative chain transfer. Dimethylaniline-MA or naphthalene-MA complexes bring about a shift of monomer ratios in the copolymer. The free radicals which contribute to the chain transfer must be predominantly of the type that have a MA unit at the end, since it is known polystyryl radicals do not react with DMA donor. These free radicals react with the DMA-MA CTC to form transfer radicals with the MA component of the CTC. Thus, a low-grade MA-MA block is formed by a reinitiation mechanism and the MA content in the copolymer increases. This supports a CTC polymerization mechanism concept, since in more polar solvents or in the presence of donor additives the amount of donor monomer-MA CTC formed would be less and the rate of copolymerization reduced accordingly. Tsuchida and coworkers,<sup>(20,21)</sup> from measured rate studies of the copolymerization of styrene with MA in a variety of solvents, support this concept and conclude that copolymerization of the styrene-MA pair clearly involves propagation in part by a CTC.

Concerning additive effects, Arnold and coworkers<sup>(1056,1057)</sup> have been looking at the starting rate of radical copolymerization of MA with styrene, using the electron spin resonance (ESR) tool and the Koelsch radical **90** as an inhibitor. The initiation rate varied with monomer compositions as a result of the decrease in the decomposition rate of AIBN initiator and a preference for the cage reaction over the formation of free radicals with increasing MA concentration. Variations in the initial rate did not change the shape of its curve on normalization of overall polymerization rate to a uniform primary radical generation rate. Inhibition by the Koelsch radical and DMA showed the presence of two different types of active chain ends.

Raetzsch<sup>(477)</sup> also discovered that the ethylene-MA pair copolymerization is not disturbed by *n*-donors, solvents, or additives; i.e., alternating materials continue to be obtained even in the presence of such additives. This could suggest the CTC formed between ethylene-MA is too strong to be disturbed by *n*-donors.





It has been pointed out that where there is an absence of dilution effects, it is hard to accept that a CTC mechanism holds. In a mixture of a donor-acceptor pair forming a CTC we have the expression

$$[\text{CTC}] = K [\text{Donor}][\text{Acceptor}].$$

By diluting the reaction by a factor of 2 the concentration of the CTC in the medium should decrease by a factor of 4:

$$[\text{CTC}] = K \frac{[\text{D}]}{2} \frac{[\text{A}]}{2}$$

Thus, dilution should decrease the relative concentration of the CTC, affecting both rates and polymer structure. Butler and coworkers<sup>(126,677)</sup> observed both a rate drop and polymer structure changes with dilution for the copolymerization of divinyl ether with MA.

As described in this chapter, strong electron donors such as vinyl ethers are readily polymerized with strong electron acceptors such as MA. Copolymerization of these systems are initiated or accelerated by photoirradiation, since the excited state CTC is polar and may give rise to ion radicals. For example, the overall rate of photoinitiated copolymerization of styrene with MA in tetrahydrofuran or acetonitrile is a maximum at 405 nm, corresponding to the absorption wavelength of the styrene-MA CTC. This indicates the possibility that the polymerization is initiated by CTC excitation.<sup>(1062)</sup> It is also known that a number of electron-donor-MA charge-transfer complexes are capable of acting as initiators or performing as photosensitizers for vinyl polymerizations.<sup>(67,295,327,352,479-482,484-487)</sup> For example, the THF-MA CTC, in the presence of light, initiates polymerization of acrylates, methacrylates, styrene, and other monomers.<sup>(348,482)</sup> It is also known that MA charge-transfer complexes can even bring about the polymerization of  $\beta$ -propiolactone.<sup>(485)</sup> The photosensitivity of charge-transfer complexes, as a general property, comes about due to interaction of the radiation with the CTC bringing it to an excited state.<sup>(443)</sup> Studies show the CTC functions in a manner similar to typical free-radical initiators; i.e., molecular weights of the polymer decreases with increasing MA-THF concentration. Ionic species are also proven to be present in some of these systems and may be used to initiate cationic polymerizations.<sup>(67,487)</sup> To expand this point, it has been observed that *N*-vinylcarbazole, in the presence of various electron acceptors, can experience



a multireaction course depending on the solvent polarity and basicity, donating property, and radical trapping ability of the acceptor and polymerizability of the electron acceptor.<sup>(442,445,488,489)</sup> This further illustrates how important a role solvents or additives may play in alternating polymerizations systems.

As explained earlier, many electron-donating and electron-accepting monomer pairs, such as *p*-dioxene-MA,<sup>(54)</sup> 1,2-dimethoxyethylene-MA,<sup>(54)</sup> vinyl sulfide-MA,<sup>(412)</sup> and styrene-MA<sup>(292)</sup> undergo spontaneous, alternating free-radical-initiated copolymerization. Park<sup>(490)</sup> attributed spontaneous or thermal polymerizations to "pseudomolecular complexes," formed between the aforesaid type monomer pairs. This follows the same general line of thought that two monomers first react to form a certain CTC and this CTC then collides with another monomer to start initiation.<sup>(491)</sup> Imoto<sup>(492)</sup> suggested the mechanism includes an initial electron transfer followed by proton transfer to give two monoradical species. Matsuda and Abe<sup>(292)</sup> claim that in solvent systems the CTC can abstract hydrogen from solvent to give biradical species. Tamura *et al.*,<sup>(1055)</sup> in their studies of the hydrogen isotope effect on the spontaneous copolymerization of MA with styrene in various solvents, support the view that the mechanism may include a CTC abstraction of hydrogen from a solvent. Gaylord and Takahashi<sup>(493)</sup> also discuss transformations of a CTC into biradical species. However, the work of Tsuchida and coworkers<sup>(291,295)</sup> with *N,N*-dimethylaniline in the styrene-MA systems and other studies do not support this concept. Electron transfer would not be favorable for weak pairs and a concept of hydrogen radical transfer is suggested as being more preferable in such cases. In several other papers,<sup>(494-500)</sup> claims have been made that the initiation center is produced noncatalytically by interaction among monomer complexes. Using spin trapping techniques and electron spin resonance studies, various free-radicals were trapped and identified in the spontaneous copolymerization of styrene and vinyl sulfides with MA.<sup>(265,313)</sup> With these results, an initiation mechanism for spontaneous copolymerization of styrene with MA was conceived.<sup>(313)</sup> The results suggest the initiating radical is formed from the CTC. A kinetic model for spontaneous copolymerization, which is readily modified to include free-radical-initiated systems, was also derived by Kokubo *et al.*<sup>(54)</sup>

The 2,3-dihydrofuran-MA copolymerization is essentially always 1:1, with the monomer composition not affected by the conversion under the copolymerization conditions  $[M_1] = [M_2]$ . This being true, the copolymerization rate can be expressed as follows (where  $[M_1] = [M_2]$  and  $R_i$  is the rate of initiation):

$$R_p = k[M_1]R_i^{1/2}$$

However, the rate of spontaneous copolymerization between 2,3-dihydrofuran and MA, at 60°C in acetone, was found to obey the following expression:<sup>(115)</sup>

$$R_p = 2.4 [M_1]^{1.99}$$

Since the equilibrium constant for the CTC of this pair is very small (Chapter 10 Appendix), the CTC concentration condition can be approximated as  $K[M_1][M_2]$  (Sec. 10.3.1). If only the CTC copolymerized the rate should be directly proportional to  $[M_1]^2$ , assuming  $[M_1] = [M_2]$ . The experimental data collected showed that the initiation rate ( $R_i$ ) was proportional to  $[M_1]^0$ , which contradicts the concept of a thermal-initiation mechanism. On the other hand, if it is assumed that the part of the order with respect to  $[M_1]$  in excess of 1 represents a higher-order initiation reaction, then the order with respect to monomer contributing to polymerization initiation should be 2. In any case, the results of  $[M_1]^{1.99}$  are not clear as to whether it is the contribution of the CTC to the growth reaction or the fit that is a result of polymerization initiation.

It would appear, depending on the electron donor–acceptor pair, that various charge-transfer complexes can give polymerization-initiating species which, under suitable circumstances may assume both free-radical and ionic character. Even though the results generally support the concept that charge-transfer interaction plays a role in generating free-radical species, a clear and unambiguous or true mechanism for spontaneous alternating-radical copolymerization is awaiting further work, especially as related to individual polymerization or copolymerization systems. Shirota and Mikawa<sup>(489)</sup> recently authored a review on thermally and photochemically induced charge-transfer polymerizations.

The monomers *N*-vinylcaprolactam (NVC), *N*-vinylpyrrolidone (NVP), *N*-vinylsuccinimide (NVS), and *N*-vinylphthalimide (NVPI), belonging to the class of *n*-donors, form nontransitory 1:1 charge-transfer complexes with MA having relatively high equilibrium constants (table in the appendix to this chapter).<sup>(170,171,172,175–179,182)</sup> There is great probability that these charge-transfer complexes, because of the higher equilibrium constants, may play a major role in alternating copolymerization of NVC, NVP, NVS, and NVPI with MA.

A CTC which experiences a strong ionic contribution in the ground state should be significantly affected by the dielectric strength of solvents, i.e., the CTC equilibrium constant should increase with dielectric strength.<sup>(10)</sup> For the NVP–MA CTC no relationship was found to exist between the dielectric constant of the medium and the equilibrium constant for CTC formation (Table 10.16). This suggests that the NVP–MA CTC experiences only a very weak ionic contribution.

Carter and coworkers<sup>(501)</sup> suggest that the effect of solvation should be taken into consideration for even weak charge-transfer complexes. In a weak CTC, the solvent may interact with either component of the CTC so that the equilibrium constant may not be a simple function of the dielectric strength of the solvent. This interpretation may apply to the results in Table 10.16.

A summary of the four *n*-donor–MA equilibrium constants and Alfrey–Price<sup>(1)</sup>  $e$  values are shown in Table 10.17. The donor–acceptor interaction



Table 10.16. NVP-MA CTC Equilibrium Constants in Various Solvents<sup>a</sup>

Solvent	Dielectric constant	$K$ (liter mole <sup>-1</sup> )
Acetone	20.70	0.007
1,2-Dichloroethane	10.40	0.119
Ethyl acetate	6.02	0.060
Chloroform	4.82	0.178
Methyl methacrylate	2.83	0.031
Benzene	2.28	0.336

<sup>a</sup> From Reference 170.

order, as shown by the equilibrium constants, is NVPI-MA < NVS-MA < NVP-MA. On the basis of these values and the  $e$  values, reaction rates would be expected to follow the same order.<sup>(65,469)</sup> As expected, the polymerization rates of the three monomer pairs in benzene and DMF, with AIBN at 65, 70, and 80°C, followed the order NVPI-MA < NVS-MA < NVP-MA. In all cases, only 1 : 1 alternating copolymers were isolated. The rates in benzene and DMF, respectively, were  $1.87 < 2.0 < 2.15$  and  $0.5 < 1.27 < 1.66$  moles/liter. These data support the previously discussed Nimoura and Susuki<sup>(469)</sup> concept.

In addition to the equilibrium constants, the rates of copolymerization of the monomers pairs in Table 10.17 were also substantially reduced in DMF. However, DMF failed to change both the reaction order and copolymer composition. The results may be partially explained by the inability of the DMF-MA CTC to coexist in the presence of the  $n$ -donor-MA pairs. The DMF-MA CTC has an equilibrium constant of 0.34 liter/mole (Table 10.15), which is not far removed from the NVPI-MA  $K$  value. Thus, it is hard to see how dilution with DMF fails to have some effect on copolymer composi-

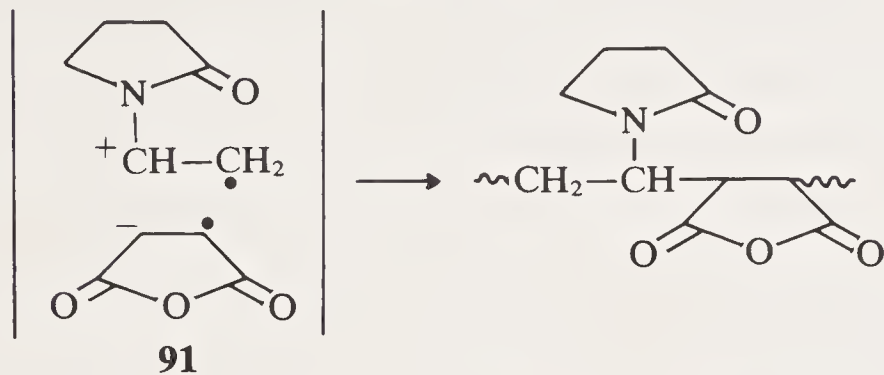
Table 10.17. NVC-, NVP-, NVS-, and NVPI-MA 1 : 1 CTC Equilibrium Constants and Alfrey-Price  $e$  Values<sup>a</sup>

Comonomer	Solvent	$K \times 10^2$ (liter mole <sup>-1</sup> )	$e$
<i>N</i> -Vinylcaprolactam (NVC)	CHCl <sub>3</sub>	20.00	-1.10
<i>N</i> -Vinylpyrrolidone (NVP)	CDCl <sub>3</sub>	120.00	-1.14
	DMF	44.20	—
<i>N</i> -Vinylsuccinimide (NVS)	CDCl <sub>3</sub>	84.60	-1.16
	DMF	9.52	—
<i>N</i> -Vinylphthalimide (NVPI)	CDCl <sub>3</sub>	76.50	-0.15
	DMF	5.24	—

<sup>a</sup> From References 41, 175, and 182.



tion. It has also been demonstrated in other systems that it is possible to have an electron-donor monomer–MA pair with too high an equilibrium constant to be disturbed by *n*-donor solvents.<sup>(241,477)</sup> The *n*-donor CTC might attach to a polymer radical more readily than a free monomer, since combination of two monomers in a CTC would contribute to a reaction with a high preexponential factor. Thus, using NVP as an example, it is thought that these reactions could occur by homopolymerization of a CTC **91**, in which the MA



residue is always an end radical. The reactions were demonstrated to be free-radical processes with activation energies of 16.7–17.3 kcal/mol and having preexponential factors of  $(1.26\text{--}20.7) \times 10^6$  liters mole<sup>−1</sup> s<sup>−1</sup>. The large variation in preexponential factor suggests these are very complex processes.

It is important to note that this is one of the very few cases where donor monomer–MA charge-transfer complexes are well characterized (Table 10.18), beyond composition, *K* value, and copolymerization effects.<sup>(171)</sup>

As shown in the table in the appendix to this chapter, the stability of a CTC decreases as polymerization temperatures are increased. Recognizing this, Seymour and coworkers<sup>(155,309,476,502)</sup> showed that for the vinyl acetate–MA, styrene–MA, and  $\alpha$ -methylstyrene–MA pairs the charge-transfer complexes were nonexistent above 90, 130, and 80°C, respectively. Above these threshold temperatures for the three charge-transfer complexes only random copolymers are produced. Fritze<sup>(305)</sup> confirmed this discovery for the styrene–MA pair. Seymour and Garner<sup>(502)</sup> recently authored a review on thermal aspects of alternating copolymerization, covering this subject.

Table 10.18. Properties of *N*-Donor–Maleic Anhydride Complexes<sup>a</sup>

Complex	$n_D^{20}$	Melting point (°C)	$\eta$ (cP)	$d_4^{20}$
MA–NVP	1.497 3	−20	3.75	1.17
MA–NVS	1.496 0	−5	3.80	1.26
MA–NVPI	1.533 0 <sup>b</sup>	34	—	1.31

<sup>a</sup> From Reference 171.  
<sup>b</sup> Complex formed at fusion temperature of 40°C. NVP- and NVS–MA complexes formed at room temperature.

All copolymerizations previously discussed have exhibited maximum rates of copolymerization at 1 : 1 monomer feed ratios, 1 : 1 copolymer compositions, and charge-transfer complexes. Also, solvents, additives, and temperature were shown to have a significant effect on the overall rates, compositions, etc., for the various systems. These facts, coupled with the observation that many of the systems undergo spontaneous and UV-induced copolymerization in the absence of initiators are all supportive of the CTC mechanism for alternating copolymerization. We now briefly discuss additional information less complementary to this mechanism.

It is usually customary to show the gross copolymerization rate as a function of the monomer composition at a constant total monomer concentration. The maximum rate at 1 : 1 feed and spectroscopic proof of the presence of a CTC is then used as partial proof that the CTC mechanism holds for a particular monomer pair copolymerization.<sup>(69,70,87,104,109,115,126,160,169,220,306,398)</sup>

This relationship need not be true. In fact, this assumption is often one of the weak points in arguing for a CTC mechanism. Raetzsch<sup>(444)</sup> points out that the maximum copolymerization rate ( $R_p$ ) for alternating copolymerization may be expressed as follows:

$$R_p = K_p[I]^y[ED]^{x_1}[EA]^{x_2}$$

After expression simplification,

$$R_p = K_p[I]^y[M]^x$$

where  $x = x_1 + x_2$  and  $M = ED \cdot EA$ .

Assuming that  $y$  is constant during copolymerization, which was demonstrated for the styrene-MA pair,<sup>(444)</sup> the maximum  $R_p$  is necessarily obtained at an equimolar ratio of the two monomers. Thus, a symmetrical curve can be obtained whose height depends on  $K_p$  and  $x$ .

Where the velocity constants for the cross-propagation reactions,  $k_{21}$  and  $k_{12}$ , are the same, the rate curve is centered at a 1 : 1 feed by assuming the addition of the CTC. This is true because the highest CTC concentration also occurs at a 1 : 1 molar ratio according to the law of mass action. Thus, the appearance of a maximum rate at a 1 : 1 monomer feed ratio does not necessarily give proof that the CTC mechanism holds. Also the appearance of a maximum rate outside of a 1 : 1 feed cannot be explained without invoking additional assumptions.

The maximum in the polymerization rate curves for isobutyl vinyl ether,<sup>(72)</sup> 2-phenylvinyl alkyl ethers,<sup>(257)</sup> 1-octene,<sup>(72)</sup> norbornene,<sup>(241)</sup> vinyl acetate,<sup>(152)</sup> butene isomers,<sup>(193)</sup> and cyclopentene<sup>(232)</sup> copolymerizations with MA are located somewhat outside the 1 : 1 feed ratios. Even though 1 : 1 copolymer is obtained, the maximum rate of styrene-MA copolymerization is normally not at 1 : 1 feed equivalency. However, Tsuchida and Tomono<sup>(20)</sup> show that addition of naphthalene causes the rate maximum point to shift



from higher concentration of MA to the equivalent concentration of MA and styrene. Schildknecht *et al.*<sup>(451)</sup> also claimed that copolymerization of both alkyl vinyl ether and styrene with MA, under varied conditions, could be controlled by reaction conditions and feed ratios. These considerations, coupled with Tsuchida and Tomono<sup>(20)</sup> showing that poly(MA) radicals may be present in styrene-MA polymerizations, cast some doubt that these polymers are strictly 1:1 alternating.

Using the  $\pi$ -extension model,<sup>(102)</sup> molecular orbital considerations of the alternating copolymerization of 4-methyl-1,3-dioxene-4 with MA have been studied.<sup>(101)</sup> Total  $\pi$  energies ( $E_\pi$ ) were calculated for the four elementary copolymerization reactions:  $\Delta E_{11} = 0.159\,9\beta$ ;  $\Delta E_{12} = 1.062\,9\beta$ ;  $\Delta E_{21} = 2.093\beta$ ; and  $\Delta E_{22} = 0.213\beta$ . The results indicate that the cross-propagation reactions,  $k_{12}$  and  $k_{21}$ , are preferred more than the homopropagation,  $k_{11}$  and  $k_{22}$ , reactions and monomer reactivities of less than unity are to be expected. There is no discrepancy with  $r_1 = k_{11}/k_{12} = 0$  and  $r_2 = k_{22}/k_{21} = 0.8-0.20$  as described by Kawai.<sup>(101)</sup> The  $\pi$ -extension model appears sufficient to account for alternating copolymerization for this pair and the method may be applicable to other systems.

Molecular orbital considerations were also recently used by Case and coworkers<sup>(153,1064)</sup> to try to describe the role played by the CTC in the alternating copolymerization of vinyl acetate (VA) with MA. Copolymerization of the two monomers was described by Eqs. (25)–(28).



The ratios  $k_{\text{ACTC}}/k_{\text{AD}}$  and  $k_{\text{DCTC}}/k_{\text{DA}}$  were estimated, respectively, as 6 and 0. This means a growing chain terminated by a  $\text{MA}\cdot$  unit adds a CTC much more readily than adding free VA. In contrast, the  $\text{VA}\cdot$  terminated macroradical does not add the CTC.

Early in the reaction, interactions between frontier orbitals play an important role. For free-radicals, the frontier orbital is the singly occupied one (SOMO). The SOMO orbital interacts with both the highest occupied orbital (HOMO) and the lowest unoccupied (LUMO) of the closed-shell substrate. Free radicals with a high-energy SOMO (nucleophilic radicals) will react fast with substrates having a lower energy LUMO, and free radicals with a lower-energy SOMO (electrophilic radicals) will react fast with a substrate with a high-energy HOMO. The HOMO in the CTC is strongly localized upon the VA moiety, which is higher than the HOMO of the VA molecule. The lowest LUMO in the CTC is strongly localized upon the MA,



which is weaker than LUMO of the MA molecule. Complexation induces a lowering of the LUMO for the VA molecule. SOMO–LUMO interactions (two orbitals, one electron) are always stabilizing. SOMO–HOMO interactions (two orbitals, three electrons) are not always stabilizing.

Using these considerations, attempts were made to explain the alternating character of the free-radical MA–VA copolymerization reaction.<sup>(153)</sup> The growing polymeric free-radical ending in VA• is adjacent to an oxygen atom, thus this radical has a high-energy SOMO; it reacts faster with a molecule having a lower LUMO energy, namely, MA. On the other hand, the growing polymeric free-radical ending in MA• is adjacent to a carbonyl group, which is a withdrawing group, thus this free-radical has a low-energy SOMO; in this case the important frontier orbital of the substrate will be its HOMO. The VA molecule has the higher-energy HOMO and is therefore the molecule that reacts with the polymer chain ending in MA• free radical. Studies by Takakura and Ranby<sup>(1113)</sup> raise questions about this concept, since electron spin resonance studies show there are possibly no VA radicals in VA–MA copolymerizations.

Caze and Loucheux,<sup>(1065)</sup> using the vinyl acetate–MA pair, have also attempted to look at the influence of a CTC between comonomers on the microstructure of the products. Nuclear magnetic resonance spectra showed no differences in configuration between two MA–vinyl acetate copolymers prepared in such a manner that a CTC would form in one system but not the other. Thermogravimetric studies did show some difference, postulated to result from differences in the conformation of the ester group. Attempts were made to explain the differences by discussing a mechanism for the participation of the CTC formation in the copolymerization.

Molar heats of polymerization or activation energy,  $-\Delta H_{\text{cop}}$  (kcal/mol) have been determined for several different alternating copolymerization systems (Table 10.19).<sup>(504,505)</sup> The values fall within the range 10–24 kcal/mol, which is normally observed for other vinyl polymerizations.<sup>(140,506)</sup> It is interesting to note, comparable activation energies are observed for maleimide copolymerization with styrene (20.9 kcal/mol) and  $\alpha$ -methylstyrene (17.2 kcal/mol).<sup>(504)</sup>

The value  $-\Delta H_{\text{cop}}$  (Table 10.19) represents a quantity  $\Delta H_{12} + \Delta H_{21}/2$  or the heat liberated by  $\frac{1}{2}$  mole of each monomer undergoing cross propagation ( $k_{12}$  and  $k_{21}$ ) to form 1 mole of polymer with alternating units in the polymer chain. It is not possible to obtain  $\Delta H_{12}$  and  $\Delta H_{21}$  directly, since the reaction represented by  $k_{12}$  and  $k_{21}$  should occur with equal frequency, i.e., steady-state assumption. However, the quantity  $-\Delta H_{\text{cop}}$  ( $\Delta H_{12} + \Delta H_{21}/2$ ) is significant when compared with the two heats of self-addition  $\Delta H_{11}$  and  $\Delta H_{22}$ . In Table 10.19, the  $-\Delta H_{\text{cop}}$  is higher than the total of the heats of self-addition for each monomer. For example, styrene self-addition ( $\Delta H_{11}$ ) is ca. 16.5 kcal/mol and MA ( $\Delta H_{22}$ ) is ca. 14 kcal/mol, compared to  $\Delta H_{12} + \Delta H_{21}/2 =$

Table 10.19. Heats of Copolymerization of MA ( $M_1$ ) With Various Comonomers  $M_2$ <sup>a</sup>

Comonomer $M_2$	$-\Delta H_{\text{cop}}$ (kcal/mol)
Styrene	$19.3 \pm 0.2$
$\alpha$ -Methylstyrene	$17.3 \pm 0.8$
Allyl chloride	$17.7 \pm 0.2$
<i>N</i> -Butyl vinyl ether	$21.5 \pm 0.2$
Vinyl acetate	$20.2 \pm 0.4$

<sup>a</sup> After Reference 504. By permission of Hüthig and Wepf Verlag, Basel, Switzerland.

19.5 kcal/mol for the copolymer. If  $\Delta H_{12}$  and  $\Delta H_{21}$  have approximately equal values it is apparent that the difference between  $\Delta H_{11} - \Delta H_{12}$  would be substantial, ranging from 3 to 6 kcal in the styrene–MA system. A substantial fraction of this type of enthalpy change contributes toward the various activation enthalpies.<sup>(507)</sup> Thus, an enthalpy difference of this magnitude (3–6 kcal) between self- and cross propagation predicts high rates of alternating copolymerization should be observed.

From a thermodynamic viewpoint, it is hard to explain why a CTC should function preferentially as a monomer during the growth step. Especially if the assumption is made that the reactivity of the CTC must be significantly higher than that of the free monomers which, according to the CTC equilibrium, are known to be present in sufficient concentration. An energy diagram shows the convergence of free monomers to the CTC is connected with release of energy.<sup>(506)</sup> The CTC is lower in energy in its ground state than the free monomers. Thus, there should be preferred addition of the free monomers as a result of the greater addition rate.

Looking at the four possible reactions for binary copolymerization, only the  $k_{21}$  and  $k_{12}$  growth steps will run their course; i.e.,  $k_{22}$  and  $k_{11}$  steps are very small or zero, if the free-radical state alone determines the alternating tendency.

Sato, Abe and Otsu<sup>(313)</sup> believe the high reactivities of the CTC can be explained by the Evans–Polanyi theory.<sup>(508)</sup> For many reactions involving radical addition and propagation of vinyl monomers, the relationship  $E = A - \alpha Q$  holds, where  $E$  is the activation energy and  $Q$  the heat of reaction.<sup>(507,509)</sup>  $A$  and  $\alpha$  are constants and the free-monomer mechanism may be visualized as follows [Eq. (29)]:



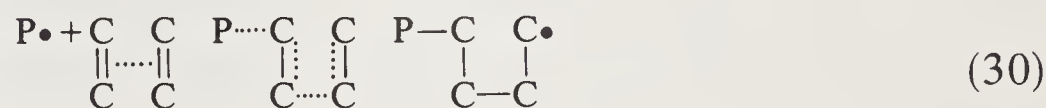
where  $P\cdot$  and  $C=C$  represent the radical and vinyl monomer, respectively.

The heat of reaction  $Q$  is calculated from the bond dissociation energies with no allowance for resonance stabilization in both monomers and radicals.



Thus, the heat of reaction is about 20 kcal/mol in which the double bond of a free monomer transforms to two single bonds. Values of 13–21 kcal/mol are common for the heats of polymerization of vinyl monomers.

In the CTC mechanism, the propagation of the free radical with the complexed monomers could be different. Two double bonds are transformed into four single bonds. The heat of reaction would be estimated to be about 40 kcal/mol for this to occur. This large value would result in a rather low activation energy for the following reaction,<sup>(313)</sup> Eq. (30):



By using the 0.4 Evans–Polanyi<sup>(508)</sup>  $\alpha$  values, the difference in activation energies of both propagations is estimated to be about 8.0 kcal/mol. On this basis, one may conclude that the rate constant of the propagating CTC is about  $6 \times 10^5$  times higher than the rate constant for the free-monomer propagation at 300 K, assuming the frequency factors are similar. Sato *et al.*<sup>(313)</sup> believe this helps explain how higher reactivities of the CTC may occur and allow CTC propagation control regardless of the low CTC concentrations. The type of monomer, charge-transfer complexes generated, growing polymer radical, solvent, etc., would play a big role in establishing the true situation.

It is well known that donor–acceptor interactions in the transition state bring about a lowering of the reaction activation energy.<sup>(507,510,511)</sup> The effect of their interactions is commonly estimated on the basis of the method of stabilization energy ( $E_s$ ). The relationship between  $E_s$  of the transition state and activation energy of the reaction ( $E_A$ ) is given by the expression  $E_A = C + E_s$ , where  $C$  is a parameter characteristic of the reacting series.<sup>(511)</sup> The value of  $E_s$  also affects the preexponential factor in the Arrhenius equation,<sup>(512)</sup> according to the expression  $A \sim E_s^2$ . Thus, the increase in value of  $E_s$  brings about an increase in the reaction rate constant. It becomes obvious that the higher the difference between  $E_s$  in the reactions or addition of a monomer to “unlike” and “like” free radicals, the stronger the tendency to alternation in the resulting copolymer should become.<sup>(28,510)</sup> For the styrene–MA pair, the calculated  $E_s$  values are given in Table 10.20.

It is apparent from Table 10.20 that  $E_s$  values for the cross-propagation reactions are noticeably higher than those for the homopropagation reactions. Therefore, cross propagation occurs to give alternating poly(styrene–co–MA).

Since kinetics do not provide a clear choice between the proposed mechanisms for alternating copolymerizations, Kabanov and coworkers<sup>(28,216)</sup> used electron spin resonance (ESR) techniques to study MA–dimethylbutadiene copolymerization. The reactions were initiated at the temperature of liquid nitrogen, using  $\gamma$  rays ( $^{60}\text{Co}$  source). The number and types of free radicals formed were studied from  $-196$  to  $-60^\circ\text{C}$ . A study of the ESR



Table 10.20.  $E_s$  Values for the Elementary Reactions of Copolymerization for the Styrene–MA Pair<sup>a,b</sup>

Reaction	$E_s^b$
St· + St	0.932 2
St· + MA	1.256 3
MA· + MA	0.826 7
MA· + St	0.093 9

<sup>a</sup> After Reference 510. By permission of John Wiley & Sons, Inc., New York, New York.  
<sup>b</sup>  $E_s$  Values in  $(\Delta\beta)^2/\beta$  units.

spectra, at various temperatures, showed that the allyl-type free radical of butadiene, maleic anion radical, and MA propagating free radical all existed. The results of this study supported the concept that in this system the alternating copolymerization involves a stepwise addition of the monomer to the growing free radical. This conflicts with the conclusion of Yamashita *et al.*,<sup>(207)</sup> on relating the microstructure of the alternating MA–butadiene copolymer to the polymerization mechanism. Since the copolymer contains essentially *cis*-1,4-butadiene moieties, in contrast to a free-radical initiated poly(butadiene) with mostly *trans*-1,4- units, a CTC mechanism is invoked to account for the observed microstructure. Gaylord *et al.*<sup>(224)</sup> also claim that the *cis*- and *trans*-1,3-pentadiene–MA CTC transformations bring about generation of only copolymer with *cis*-1,4-pentadiene units.

Using the low-energy  $\beta$  ray from radioactive carbon (<sup>14</sup>C) and  $\gamma$  rays from radioactive chlorine (<sup>38</sup>Cl), quantitative analysis of the end groups of styrene–MA copolymers have been studied by tracer and activation analysis techniques.<sup>(303)</sup> Using carbon tetrachloride and chloroform solvents and initiators containing <sup>14</sup>C, the initiation, chain-transfer, and termination mechanisms were clarified for this system. The techniques used gave estimates of initiator fragments and chlorine content in the copolymer. The results infer that copolymerization only occurs when the primary free-radical directly attacks monomer and that of hydrogen abstraction by the primary free-radical or initiation by trichloromethyl radical could hardly occur. Only a slight amount of chlorine, one per 12–15 copolymer chain molecules, were incorporated into the copolymer, substantially less than normally observed for telomerization reactions. Since initiation and chain transfer to solvent do not appear to have much influence on the results of the reaction, the authors<sup>(303)</sup> conclude that chain transfer to the comonomer is violent and growing free radicals do not react easily with the acceptor solvent carbon tetrachloride. Even when the growing free radical is attached to styrene, because of the

dominance of the reaction with free monomer or CTC, the carbon tetrachloride solvent has little influence. These results agree with earlier studies<sup>(20)</sup> and are not incompatible with either the free monomer, CTC, or combination of these two mechanisms.

Spirin and Yatsimirskaya<sup>(312)</sup> studied the kinetics of styrene-MA copolymerization in acetic anhydride by a dilatometric method. The order of the reaction, with respect to the monomer concentration, was close to 0.5, with the reaction rate increasing as the proportion of MA increased. This supports a mechanism of alternating copolymerization occurring by successive addition of free monomer. CTC participation is not precluded. However, it is believed the CTC plays only a minor role due to their low concentrations. In contrast, kinetic studies and potentiometric titrations have led others<sup>(306)</sup> to suggest that homopolymerization of the CTC occurs.

Of all the MA copolymerizations studied, the MA-styrene pair has perhaps received the greatest attention in an attempt to understand the mechanism of alternating copolymerization.<sup>(315)</sup> For this pair, the understanding is complicated by the fact that styrene-rich copolymers can be prepared from styrene-rich feeds. Bamford and Barb<sup>(280)</sup> studied the copolymerization of the styrene-MA pair in several solvents and Barb<sup>(282)</sup> interpreted the kinetics of the reaction in terms of a penultimate group (i.e., unit adjacent to the radical end group) effect operating on polymer free radicals with a terminal styrene unit. Enomoto *et al.*<sup>(299)</sup> after studying the same reaction under pressure, invoked the same concept of penultimate group effect to account for the observed kinetics.

Ang and Harwood,<sup>(287)</sup> after sequence distribution measurements by NMR, claimed the MA-styrene-MA triads were in excellent agreement with the result predicted by the "terminal" model reactivity ratios,  $r_1 = 0.019$  and  $r_2 = 0$  and in poor agreement with Barb's<sup>(282)</sup> penultimate reactivity ratios of  $r_1 = 0.017$  and  $r_2 = 0.063$ . As mentioned earlier, Tsuchida and coworkers<sup>(20,21)</sup> studied the copolymerization of this pair and concluded that propagation progressed, in part, via a 1 : 1 styrene-MA CTC. Farmer *et al.*<sup>(1049)</sup> claim the complex model accounts for the copolymerization data collected on the bulk-phase, free-radical polymerization of the styrene-MA pair. Seiner and Litt<sup>(428)</sup> also suggested that the marked deviations from the classical kinetic scheme of Mayo and Lewis<sup>(513)</sup> and Alfrey and Goldfinger,<sup>(514)</sup> observed for this pair, constituted additional evidence for charge-transfer complexes playing a role in the copolymerization. Seymour and coworkers<sup>(155,476,502)</sup> collected evidence that the charge-transfer complex has a threshold temperature, above which only random copolymer could be obtained. Otsu and coworkers<sup>(265,313)</sup> identified the initiating and propagating free-radicals for this system, by spin trapping techniques, supported the Litt and Seiner<sup>(428b)</sup> concept. Yoshimura *et al.*<sup>(515)</sup> claimed that propagation by charge-transfer complexes is significant in other systems.



Recognizing all the above, Dodgson and Ebdon<sup>(314)</sup> initiated a comprehensive study to test whether a mechanism involving a 1 : 1 styrene–MA CTC propagation could satisfactorily account for the observed dependence of copolymer composition upon monomer feed, which was previously attributed to penultimate group effects. Kinetics of the free-radical copolymerization of the pair were studied both neat and in several solvents at 60°C and to low conversions. The results and conclusions of this study follow.

The styrene–MA CTC, with a 1 : 1 stoichiometry, appeared not to be very solvent dependent (Table 10.21). Various solvent–MA charge-transfer complexes also exhibit 1 : 1 stoichiometry. The addition of diphenylpicrylhydrazyl, at several concentrations, gave overall kinetics consistent with a straight-forward free-radical polymerization mechanism.

Attempts to obtain simple reactivity ratios from composition data by various techniques<sup>(516,517)</sup> led to the conclusion that the kinetics of the styrene–MA copolymerization do not follow the classical scheme of Mayo–Lewis<sup>(513)</sup> and/or Alfrey–Goldfinger.<sup>(514)</sup> All systems gave rise to Fineman–Ross<sup>(516)</sup> and Kelen–Tudoz<sup>(517)</sup> plots with pronounced curvature. Barb<sup>(282)</sup> type plots also exhibited substantial curvature, contrary to classical kinetic predictions. The kinetic abnormality was clearly similar to that previously reported<sup>(282)</sup> and attributed to a penultimate group effect. Barb<sup>(282)</sup> postulated that a styryl free radical bearing a penultimate MA unit was less reactive toward MA monomer than a styryl free radical bearing a penultimate styrene unit, following the Mertz–Alfrey–Goldfinger concept.<sup>(518)</sup> Their observations agree with the conclusions of Ogo and Imoto<sup>(519)</sup> on the penultimate effect of styrene–MA copolymerizations under high pressure. The calculated penultimate reactivity ratios (Table 10.22) gave best agreement with the observed copolymer compositions.

Comparison of the calculated penultimate and CTC reactivity ratios allowed two important observations. First, it is believed that if the participation

Table 10.21. Equilibrium Constants for MA Charge-Transfer Complexes<sup>a,b</sup>

Complex	$K$ (liter mole <sup>-1</sup> )
Styrene–MA	0.25 <sup>a</sup>
MA–2-butanone	0.62
Styrene–2-butanone	0.07
Styrene–chloroform	0.15
MA–chloroform	0.14
Styrene–dimethylsulfoxide	0.15
MA–dimethylsulfoxide	1.32

<sup>a</sup> After Reference 314. By permission of Pergamon Press Ltd., Headington Hill Hall, Oxford, England.

<sup>b</sup> All  $K$  values determined in cyclohexane at 60°C.



Table 10.22. Penultimate Reactivity Ratios for Styrene-MA<sup>a</sup>

Solvent	$r_{\text{MSM}}$	$r_{\text{SSM}}$
None	1.50	0.011
Chloroform	0.85	0.022
Methyl ethyl ketone	0.23	0.027
Dimethylsulfoxide	0.95	0.024

<sup>a</sup> After Reference 314. By permission of Pergamon Press Ltd., Headington Hill Hall, Oxford, England.

of the styrene-MA CTC is to explain the observed kinetics of alternating copolymerization then the CTC must have a higher reactivity toward a styryl free radical than either free styrene or free MA. Second, the CTC must be essentially equally reactive at both its styrene and MA sides toward a styryl free radical. Dodgson and Ebdon<sup>(314)</sup> point out that it is doubtful this can be true. Precluding large-scale rearrangement of electronic energy levels, the CTC should be most reactive at its MA side. Styryl-radical attack should occur at this location since greater donor-acceptor interactions in the transition state would occur and also greater resonance stabilization should be realized by the resulting styryl free radical.

According to the CTC mechanism, copolymerization kinetics should be less and less influenced by the CTC as overall monomer concentrations are reduced, i.e., dilution effect. For the styrene-MA pair, the CTC model failed to adequately account for only small changes observed in copolymer composition when the overall monomer concentration was changed by a factor of 16.

For copolymerizations involving significant propagation of a CTC, the addition of a compound that enhances formation of the CTC or that preferentially complexes with one of the monomers would be expected to show a marked effect on both the rate of formation and composition of the copolymer.<sup>(438,441,444)</sup> According to this concept  $\text{ZnCl}_2$  addition would be expected to lead to increased complexation between styrene and MA and thereby enhance the already high alternating tendency. The effect was opposite:  $\text{ZnCl}_2$  addition lowered the amount of MA incorporated in the copolymer. These results are more in accord with a penultimate model than with the CTC model. The opposite has been found true for electrochemical and sodium naphthalene initiated copolymerization of styrene with diethyl fumarate.<sup>(483)</sup> Equimolar copolymer is obtained in both cases on addition of  $\text{ZnCl}_2$  to the polymerizing systems.

The phthalic anhydride-styrene CTC equilibrium constant, determined in 2-butanone at 60°C, is 0.23 liter mole<sup>-1</sup>. According to the CTC mechanism concept, if phthalic anhydride were added to the styrene-MA system one

would expect to observe both a reduction in rate and change of copolymer composition. Addition of 10 and 20 mol % of phthalic anhydride showed a slight rate enhancement with a corresponding slight drop of MA incorporation in the copolymer. These effects are not well understood nor are they in line with a CTC mechanism.<sup>(314)</sup>

From the observation briefly discussed above, Dodgson and Ebdon<sup>(314)</sup> gave five reasons why it is not likely that the copolymerization of the styrene–MA pair in normal solvents involves significant contribution of a CTC between the two monomers.

1. The overall kinetics of the copolymerizations conform to a straightforward free-radical process.
2. The styrene–MA CTC would need to be equally reactive toward styryl free radical on both its styrene and MA side to account for the observed composition of the copolymers.
3. Significant changes in overall monomer concentration have negligible effects upon copolymer composition.
4. Addition of  $\text{ZnCl}_2$  to the system leads to reduction of MA in the copolymer.
5. The observed rates of copolymerization are sensitive to the overall nature of the medium and cannot be interpreted simply in terms of the effect of a styrene–MA CTC.

Observations by Raetzsch *et al.*<sup>(536)</sup> from various olefin–MA copolymerizations support the above conclusions. They feel that it is not necessary to assume a monomer CTC in the propagation step to account for observed results, and from an energy point of view, the formation of charge-transfer complexes with low enthalpy of formation does not seem probable.

Farmer *et al.*<sup>(1049)</sup> recently used the Dodgson–Ebdon<sup>(314)</sup> data to reevaluate styrene–MA copolymerization. It was shown that the complex model could account for the copolymer composition data.<sup>(1049)</sup> Evidence was also uncovered to suggest that MA sequences could be formed in systems with high MA feed concentrations.

## 10.5. TERNARY COPOLYMERIZATIONS

Monomer reactivity ratios (see Chapter 9), obtained from binary copolymerization, have long been used for comparison of the reactivities of monomers toward reference polymer radicals.<sup>(538)</sup> However, the same procedure is unreliable for polymer radicals showing very low reactivities toward their own monomer. Ham<sup>(531,539)</sup> pointed out that in such cases, which includes MA, useful information may be obtained from terpolymerization studies.



Alfrey *et al.*<sup>(542)</sup> developed triangular diagram concepts and equations to help make it possible to find a quantitative relationship between the composition of the monomer mixture and the terpolymerization product. Also, the analysis of terpolymerizations may be achieved by the traditional copolymerization theory of Alfrey–Goldfinger,<sup>(540)</sup> based on nine elementary reactions and assuming alternating growth is fast. Walling *et al.*<sup>(17)</sup> applied these theories to ternary systems composed of monomers not inclined to homopolymerize, i.e., two types of substituted  $\alpha$ -methylstyrene and MA. They found the traditional theory could not explain the copolymerization characteristics of an electron-donating monomer with an electron-accepting monomer. After studying the *p*-dioxene–MA–acrylonitrile ternary mixture, Iwatsuki and Yamashita<sup>(94)</sup> also concluded it was not possible to use the known theory<sup>(540)</sup> of ternary polymerizations to explain the observations that the donor–acceptor pair was always incorporated in a 1 : 1 fashion in the polymer.

Since binary copolymerization studies contain a good measure of uncertainties when trying to prove the concept that a propagating CTC plays a decisive role in alternating copolymerizations, a number of research groups have looked at MA terpolymerizations (Tables 10.23 and 10.24) to provide additional clarification and/or support for this mechanistic concept. To do this, these groups have looked at modifying the conventional copolymerization equation to accommodate possible donor–acceptor–neutral, didonor–mono-acceptor, and monodonor–diacceptor monomer combinations to give additional understanding of the possible role of charge-transfer complexes in alternating copolymerizations. A brief discussion of these studies and conclusions are provided.

#### 10.5.1. Donor–Acceptor–Neutral Monomer Combinations

With the goal of ascertaining if observable charge-transfer complexes, between donor monomers and the strong electron-acceptor monomer MA, can act as a single monomer in alternating polymerizations, a number of groups have studied donor–acceptor–neutral monomer ternary mixtures (Table 10.23). Donor monomers have consisted of ethylene, allyl chloride,  $\alpha$ -methylstyrene, cyclopentene, bicyclo[2.2.1]-heptene-2, styrene, anethole, 2-chloroethyl vinyl ether, *p*-dioxene, 1,3-cyclooctadiene, *p*-oxathiene, and *N*-vinylpyrrolidone (NVP). Neutral monomers studied have included acrylonitrile, methacrylonitrile, methyl methacrylate, and 2-chloroethyl methacrylate. It is interesting to point out, in cases where the donor monomer may be an amide, such as NVP, initiators may not be needed to achieve terpolymerization.<sup>(169,170)</sup> In these cases, it is possible for the amide–MA CTC, with heat or UV irradiation, to initiate the polymerization.

Acrylonitrile has been used most often as a neutral monomer, since it behaves well in this function and is both readily identified and quantified in



Table 10.23. MA Terpolymerizations with Donor and Neutral Monomers; Apparent and True Reactivity Ratios

Donor monomers	Neutral monomers (N)	Apparent reactivity ratios		True reactivity ratios		References
		$r_1K$ (liter mole <sup>-1</sup> )	$r_2K^{-1}$ (mole/liter)	$r_1$ (complex)	$r_{2(N)}$	
Styrene	Methyl methacrylate	—	—	—	—	19, 528, 529
Styrene	Methyl acrylate	—	—	—	—	19
<i>p</i> -Dioxene	Acrylonitrile	4.50 ± 1.0	0.23	—	—	54, 94
<i>p</i> -Dioxene	Acrylonitrile	3.4	0.28	5.0	0.189	419, 466
Isobutyl vinyl ether	Methyl methacrylate	—	—	—	—	135
<i>N</i> -Buyl vinyl ether	Acrylonitrile	—	—	83.00	0.009	1068
2-Chlorethyl vinyl ether	Acrylonitrile	1.52	0.385	—	—	473
2-Chloroethyl vinyl ether	Acrylonitrile	1.25	0.36	4.8	0.09	419, 466
Divinyl ether	Acrylonitrile	—	—	—	—	126, 523
Anethole	2-Chlorethyl methacrylate	0.495	2.21	11.5 ± 1.2	0.095	358
Anethole	Methacrylonitrile	1.280	0.64	29.8 ± 2.6	0.028	358
Anethole	Acrylonitrile	1.937	0.16	45.0 ± 2.9	0.007 0	358
Anethole	Vinylidene chloride	2.30	0.14	53.5 ± 6.1	0.006 0	358
Styrene	Vinylidene chloride	—	—	—	—	1075
Styrene	Acrylonitrile	—	—	—	—	236, 1144
Ethylene	Acrylonitrile	0.74	1.9	—	—	236
Cyclopentene	Acrylonitrile	0.70 ± 0.2	2.5 ± 0.4	23.8 ± 8	0.75 ± 0.01	236
Norbornene	Acrylonitrile	0.30	2.0	20.0	0.03	236
4-Vinylcyclohexene	Acrylonitrile	—	—	—	—	99, 547
1,3-Cycloheptadiene	Acrylonitrile	—	—	—	—	252
1,3-Cyclooctadiene	Acrylonitrile	1.88	0.12	—	—	259
<i>N</i> -Vinylpyrrolidone	Methyl methacrylate	17.2 ± 7.4	0.055 ± 0.015	555 ± 240	0.001 7 ± 0.000 5	169, 170
<i>p</i> -Dioxene	Chlorethyl acrylate	2.3 ± 0.5	0.48 ± 0.05	—	—	96
<i>p</i> -Oxathiene	Acrylonitrile	1.4 ± 0.3	0.7 ± 0.25	55.8	0.017 6	419
$\alpha$ -Methylstyrene	Acrylonitrile	—	—	—	—	548
Allylchloride	Acrylonitrile	—	—	—	—	549

the isolated copolymers. MA–acrylonitrile copolymerization studies, in a variety of solvents and with added complexing agents, have shown that polymerization of this pair obeys the Mayo–Lewis<sup>(513)</sup> copolymerization equation. In addition, it is known that acrylonitrile–MA CTC formation need not drastically affect the copolymerization constants for this comonomer pair.<sup>(543)</sup>

Failure of traditional copolymerization equations to predict the composition of the terpolymers from donor–acceptor–neutral monomer ternary mixtures brought about the thought that these systems might be amenable to evaluation as copolymerization of a CTC (complexomer) with neutral monomer.<sup>(539,540,542,545)</sup> In other words, polymerization of a three monomer mixture, consisting of an electron-donor monomer, electron-acceptor monomer (MA), and a neutral monomer could be considered as a binary copolymerization of the complexomer ( $M_1$ ) with a neutral monomer ( $M_2$ ). Using this technique, the polymer could be analyzed as a two-component system, assuming the CTC played a decisive role in the copolymerization.

The common composition formula for binary polymerization takes the form of Eq. (31).

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]} \left[ \frac{r_1[M_1] + [M_2]}{[M_1] + r_2[M_2]} \right] \quad (31)$$

To expand this Mayo–Lewis<sup>(513)</sup> expression to accommodate the CTC we use the following relationships:

$$[M_1] = K[\text{Donor monomer}][\text{MA}]$$

$$[M_2] = \text{Neutral monomer}$$

Having done the above, we obtain Eq. (32) for the copolymerization of the complex with neutral monomer,

$$\frac{d[M_1]}{d[M_2]} = \frac{[D][MA]}{[N]} \left[ \frac{r_1 K [D][MA] + [N]}{[D][MA] + r_2 K^{-1} [N]} \right] \quad (32)$$

where D stands for donor monomer, MA for maleic anhydride, and N for neutral monomer in the feed or polymers. In Eq. (32), the CTC equilibrium constant ( $K$ ) reduces the initial concentration of the donor  $[D]$  and acceptor  $[MA]$  to the effective CTC concentration.

Using Eq. (32) and feed and terpolymer composition data, a copolymerization composition diagram can be drawn, compared with the theoretical curves, and the coefficients of the Mayo–Lewis<sup>(513)</sup> equation,  $r_1 K$  and  $r_2 K^{-1}$ , estimated (Table 10.23). Fineman–Ross<sup>(516)</sup> plots may also be used to estimate the Mayo–Lewis coefficients. These dimensioned apparent or modified reactivity ratios deviate from the “true” reactivity ratio values the more greatly the equilibrium constants differ from unity.



For the *p*-dioxene–MA pair copolymerization with 2-chloroethyl acrylate (Table 10.23) the  $r_1K$  (CTC) = 2.3 and  $r_2K^{-1}$  (2-chloroethyl acrylate) = 0.48 values describe the copolymerization results. In addition, for use of either 2-chloroethyl acrylate or acrylonitrile the product of the  $r_1Kr_2K^{-1}$  values were approximately 1. The  $r_1Kr_2K^{-1}$  value for the NVP–MA–methyl methacrylate system (Table 10.23) is also approximately 1. The data from these copolymerizations suggest a strong tendency exists for ideal polymerization (see Chapter 9). These results also support the concept that the copolymerizations take place between the *p*-dioxene–MA and NVP–MA charge-transfer complexes and the respective neutral monomers.<sup>(96,169,170)</sup>

The CTC and neutral-monomer reactivity ratios may change both by dilution and with the nature of the solvent. For example, in the *p*-dioxene–MA–acrylonitrile system in benzene or toluene, the acrylonitrile content in the polymer increased to a maximum and then decreased as the amount of solvent increased.<sup>(259)</sup> The observed solvent effects support the concept that when a CTC becomes solvated with a  $\pi$ -electron-rich solvent the CTC becomes stable to free-radical attack.

Solvent effects were also noted in the 1,3-cyclooctadiene–MA–acrylonitrile polymerizations.<sup>(259)</sup> The acrylonitrile content of the polymer was dependent on the solvent employed, showing increasing incorporation in the order 2-butanone > benzene > chloroform. However, the ratio of 1,3-cyclooctadiene to MA remained 1:1 and did not depend on acrylonitrile content. The donor tendency of the solvents, specific monomer–solvent interactions, etc., could also have caused variation of acrylonitrile in the polymers.

Using the CTC equilibrium constants (table in the appendix to this chapter) it is possible to calculate the true reactivity values for the CTC and for the neutral monomer. Raetzsch and coworkers<sup>(236)</sup> used this procedure for the cyclopentene–MA and norbornene–MA copolymerizations with acrylonitrile (Table 10.23). The same technique was also used to determine the reactivity constants for several other donor–acceptor–neutral monomer polymerizations (Table 10.23). For the NVP–MA–methyl methacrylate system the true reactivity ratios show the NVP–MA CTC is about 3 000 times the reactivity of NVP and 600 times the reactivity of methyl methacrylate toward the propagating radical ending in methyl methacrylate.<sup>(170)</sup> Results of this type support the concept of alternating copolymerization of a CTC with neutral monomer.

Considering the CTC as a single monomer, it is possible to estimate  $Q$  and  $e$  values for the charge-transfer complexes. This was done for the anethole–MA pair.<sup>(358)</sup> The  $Q$  and  $e$  values for the complex vary widely with the neutral monomer and  $Q$  is very large in comparison to typical  $Q$  values for vinyl monomers. Similar observations have been reported for Lewis acid complexes of polar vinyl monomers.<sup>(494)</sup> Since  $Q$  values are envisioned as being enhanced by resonance energy on going from a monomeric state to a



free-radical state, the very large  $Q$  values may relate to the pronounced reactivity of the CTC. Apart from this possibility, the significance of the  $Q$  and  $e$  values of the CTC is not readily understood.

Use of the modified copolymerization reactivity ratios for the quantitative description of the system where the CTC is considered to copolymerize with the neutral monomer does not serve to prove the concept that the CTC acts as an independent monomer and controls propagation. The method serves only as a mathematical model to describe the initial and final state of the system. Also, the concept is useful to assign a reactivity to the CTC, which is assumed to be an active species. However, whenever the equimolar ratio of donor monomer–MA is distributed in the polymer a dominant role cannot be envisioned for the CTC in the propagation step.

It is thought that even if the donor monomer–MA ratio is not altered by feed ratios it is still possible that the CTC and the free monomer themselves can both react with the third neutral monomer. No doubt this explains how deviations in the molar equivalency occurs in the (styrene–MA)–methyl methacrylate,<sup>(528)</sup> and (norbornene–MA)–acrylonitrile<sup>(236)</sup> systems.

For those systems where 1:1 incorporation of the CTC pair appears to always occur, i.e., (cyclopentene–MA)–acrylonitrile,<sup>(236)</sup> (ethylene–MA)–acrylonitrile,<sup>(236)</sup> (*p*-dioxene–MA)–acrylonitrile,<sup>(54,94)</sup> (*N*-vinylpyrrolidone–MA)–methyl methacrylate,<sup>(170)</sup> (*p*-dioxene–MA)–2-chloroethyl acrylate,<sup>(96)</sup> (1,3-cyclooctadiene–MA)–acrylonitrile,<sup>(259)</sup> and (anethole–MA) with acrylonitrile, methacrylonitrile, or 2-chloroethyl acrylate,<sup>(358)</sup> the event can possibly be explained by assuming that each free-radical has acceptor properties. Raetzsch *et al.*<sup>(236)</sup> discuss this concept.

The equilibrium constants for the CTC of cyclopentene, norbornene, and styrene monomers with MA are 0.03, 0.015, and 0.33 liter mole<sup>-1</sup>, respectively (table in the appendix to this chapter). However, when these three pairs are copolymerized with acrylonitrile only the cyclopentene–MA pairs remain equimolar at all feeds. This shows the CTC does not always have to be the most reactive species in the systems. Even though charge-transfer complexes are present in a ternary mixture of MA–methyl methacrylate–methyl acrylate they have little influence on the propagation kinetics.<sup>(29)</sup> The equilibrium constants for the MA–methyl methacrylate and methyl acrylate–MA pairs are 0.43 and 0.32 liter mole<sup>-1</sup>, respectively. Since these CTC equilibrium constants are comparable to many of the other donor monomer–MA pairs reported to undergo alternating copolymerization, these results are definitely nonsupportive of a CTC mechanism.<sup>(29)</sup>

Results from these donor monomer–MA–neutral monomer copolymerizations allow different opinions. Some claim their results support the concept of a significant or decisive role for the CTC in the propagating mechanism.<sup>(94,96,98,170,358,460,466,523,551,552,1062)</sup> Others claim their results are best described by a mixed CTC and free-monomer mechanism.<sup>(19,228,236,371,536,1063,1067,1144)</sup> The latest work by Dodgson and

Ebdon<sup>(29,529)</sup> on the terpolymerization of the styrene–methyl methacrylate–MA system, tends to discount any role for the CTC. They suggest their results support the importance of a penultimate group effect involving the styryl radicals. Matsuda *et al.*<sup>(560)</sup> in their studies on styrene sulfur dioxide–methyl methacrylate copolymerizations, rule out participation of the styrene–sulfur dioxide complex in the propagation reaction. These results conflict with the results of Barb. Clearly, various mechanisms appear to be operating in most of these ternary copolymerizations.

### 10.5.2. Donor<sub>1</sub>–Donor<sub>2</sub>–Acceptor Monomer Combinations

Examples of donor<sub>1</sub>–donor<sub>2</sub>–acceptor (MA) combinations that have been studied are recorded in Table 10.24. Here again, these studies were anticipated to provide a clearer picture concerning the existence and role of a CTC in alternating copolymerizations. Where two donor monomers and one acceptor monomer coexist in the same medium, two different charge-transfer complexes may be formed with both containing the acceptor as a common constituent, Eqs. (33) and (34).



If the terpolymerizations in Table 10.24 occur through the polymerization of the two complexomers (D<sub>1</sub>A<sub>1</sub> and D<sub>2</sub>A<sub>1</sub>) instead of following the classical copolymerization equations, the resulting polymers should contain 50% of the acceptor, which is common to both charge-transfer complexes. In many of the terpolymerization recorded in Table 10.24 polymers with a molar composition of 50% MA were observed, regardless of the feed mixtures.<sup>(75,130,132,228,293,384,402,405,527)</sup>

As explained earlier, Alfrey and Goldfinger<sup>(540)</sup> used nine propagation reactions to make possible a quantitative prediction of the polymerization characteristics of a three-component system of monomers M<sub>1</sub>M<sub>2</sub>M<sub>3</sub>, where the reactivity ratios of the three pairs (M<sub>1</sub>–M<sub>2</sub>, M<sub>1</sub>–M<sub>3</sub>, and M<sub>2</sub>–M<sub>3</sub>) are known. If two of the monomers in these systems are very resistant to radical-initiated polymerization, the expressions correlating the composition of the polymer and the feed take on the form of Eqs. (35)–(37).

$$\frac{m_1}{m_2} = 1 + \frac{r_{12}M_1}{M_2} + \frac{r_{12}M_3}{r_{13}M_2} \quad (35)$$

$$\frac{m_1}{m_2} = 1 + \frac{r_{13}M_1}{M_3} + \frac{r_{13}M_2}{r_{12}M_3} \quad (36)$$

$$\frac{m_2}{m_3} = \frac{r_{13}M_2}{r_{12}M_3} \quad (37)$$



Using the reactivity ratios for the various monomeric pairs, the aforesaid assumption was tested for the didonor system consisting of *N*-vinylphthalimide, (NVPI)-*n*-butyl vinyl ether (BVE), and NVPI- $\alpha$ -methylstyrene copolymerization with MA.<sup>(175)</sup> In both cases, modified Eqs. (35)–(37) failed to describe the terpolymer compositions. For all feed ratios the polymers contained the MA–BVE and MA– $\alpha$ -methylstyrene, pairs in close to 1 : 1 ratio, which is not predicted by the equation. Also, the polymerization reactions were significantly accelerated by an increase in the total concentration of an equimolar mixture of the two complex pairs and/or the amount of MA in the mixture increased. Significant deviations from the classical concepts for copolymerizations were also observed for other systems in Table 10.24.

Assuming the copolymerization data showed the NVPI ( $M_1$ ) copolymerized with charge-transfer complexes of the two other donor–MA ( $M_2$ ) pairs, modified reactivity ratios were determined for the two systems.<sup>(175)</sup> The reactivity ratios for the NVPI ( $M_1$ )– $M_2$  (BVE–MA) and  $M_1$ – $M_2$  ( $\alpha$ -methylstyrene–MA), respectively, were  $r_1 = 0.16$  and  $r_2 = 1.09$  and  $r_1 = 0.30$  and  $r_2 = 1.70$ . A copolymerization curve with these modified reactivity ratios more adequately described the observed copolymer compositions than the classical concept.

Following the Alfrey–Price<sup>(1)</sup> scheme, the charge transfer complexes in the copolymerization reactions were characterized by their  $Q$  and  $e$  values. Using the known NVPI values ( $Q = 0.07$  and  $e = -0.15$ ),<sup>(41)</sup> the estimated values for BVE–MA ( $Q = 0.36$  and  $e = 1.17$ ) and  $\alpha$ -methylstyrene–MA ( $Q = 0.10$ ,  $e = 0.67$ ) were determined. These results confirm the concept that the charge-transfer complexes should readily copolymerize with NVPI.<sup>(175)</sup>

MA–allyl alcohol (Table 10.25) and MA–methallyl alcohol (Table 10.26) pairs have been combined with a variety of other donor-type monomers and polymerized with radical initiators.<sup>(45,556)</sup> In all these cases, classical terpolymer copolymerization equations also failed to describe the resultant polymers. Sackman and Kolb<sup>(45)</sup> suggest their studies on MA–allyl alcohol (Table 10.25) or methallyl alcohol (Table 10.26) copolymerizations, with other donor monomers, supported the assumption that a CTC may participate in the propagation reactions.

For the styrene–vinyl acetate–MA polymerization very significant deviations from the classical concept of free-radical copolymerization were observed.<sup>(149)</sup> Due to almost identical rates of reaction of MA with styrene and vinyl acetate, there is strict alternation of the monomers along the polymer chain and the copolymer composition regularly corresponds to a 1 : 1 : 1 ratio.

Additional consideration of the previously mentioned complexomer–complexomer copolymerization concept dictates that the highest yields and maximum rates of copolymerization should occur in these systems as a



Table 10.24. Maleic Anhydride Terpolymerizations with Donor<sub>1</sub>-Donor<sub>2</sub> Monomers

Donor monomer 1	Donor monomer 2	Relative (Modified) Reactivity Ratios		References
		$r_1 K_I / K_{II}$	${}_2 K_{II} / K_I$	
4-Methyl-1,3-dioxene-4	Styrene	—	—	101
2-Vinyl-1,3-dioxene	Styrene	0.10	7.40	130, 132
Ethylene	Vinyl chloride	—	—	384
2-Chloroethyl vinyl ether	<i>p</i> -Dioxene	2.23	0.45	552
2-Chloroethyl vinyl ether	<i>p</i> -Dioxene	2.05	0.34	466
2,5-Dihydrofuran	Styrene	0.30	6.30	20
Cyclohexene	Styrene	0	22.32	20
<i>N</i> -Vinylphthalimide	<i>n</i> -Butyl vinyl ether	0.16	1.09	175
<i>N</i> -Vinylphthalimide	$\alpha$ -Methylstyrene	0.30	1.70	175
2-Chloroethyl vinyl ether	Styrene	0.30	2.54	20, 75
2-Chloroethyl vinyl ether	2,5-Dihydrofuran	2.78	0.52	20, 75
Vinyl chloride	Butadiene	—	—	385
Styrene	Vinyltriethoxysilane	15.1	0.115	402, 405, 553
Styrene	Vinyl Acetate	—	—	149
Styrene	4-Cyanocyclohexene	0.406	0.366	527
4,5-Epoxy-4-methyl-1-pentene	Styrene	—	—	228
Styrene	Tributyl stannyl methacrylate	8.1	1.10	402, 405, 553
Isobutyl vinyl sulfide	Isobutyl vinyl ether	5.6	0.20	554
Ethyl vinyl sulfide	Ethyl vinyl ether	4.0	0.20	554
Indene	2,3-Benzofuran (coumaran)	—	—	410, 555
<i>p</i> -Oxathiene	2-Chloroethyl vinyl ether	0.60	1.65	419
<i>p</i> -Oxathiene	<i>p</i> -Dioxene	0.42	0.36	419
Vinyl ferrocene	Styrene	—	—	410

Table 10.25. MA-Allyl Alcohol Copolymerization With Other Donor Monomers<sup>a</sup>

Donor monomer <sup>b</sup>	Yield (%)	$[\eta]$ (dl/g)	Polymer melt temperature (°C)
2-Chloroprene	64.6	0.095	>145
Allyl chloride	60.7	—	110–140
Methallyl acetate	84.8	0.098	>157
Allyl acetate	52.8	0.109	115–170
Ethylene	64.6	0.110	>108
Allyl ethyl ether	85.2	—	95–115
Cyclopentene	81.3	—	130–180
1-Butene	81.1	—	>120
Diisobutylene	56.1	—	95–115
$\alpha$ -Methylstyrene	81.3	0.141	<202
Indene	94.6	0.158	<194
Styrene	93.4	0.20	>135

<sup>a</sup> After Reference 45. By permission of Hüthig and Wepf Verlag, Basel, Switzerland.<sup>b</sup> Copolymerizations run under N<sub>2</sub> in dioxene at 70°C, using 1.0 wt. % AIBN initiator.

D<sub>1</sub>:D<sub>2</sub>:Acceptor ratio of 1:1:2. This was observed for the 4,5-epoxy-4-methyl-1-pentene (EMP):styrene:MA combination.<sup>(228)</sup> Thus, the two charge-transfer complexomers (EMP-MA and styrene-MA) were believed to play a decisive role in the chain-propagation reactions. The anhydride content in the polymer was ca 0.50 mol % and almost completely independent of MA in the feed. The total activation energy ( $E_a$ ) for this binary copolymeri-

Table 10.26. MA-Methallyl Alcohol Pair Copolymerization with Other Donor Monomers<sup>a</sup>

Donor monomer <sup>b</sup>	Yield (%)	$[\eta]$ (dl/g)	Polymer melt temperature (°C)
Cyclopentene	96.0	0.110	>130
Allyl chloride	77.4	—	150–175
$\alpha$ -Methylstyrene	64.6	0.119	>125
Ethylene	80.3	0.130	<120
Diisobutylene	94.3	0.157	<190
Methallyl acetate	97.0	0.171	<164
1-Butene	92.9	0.196	<140
Vinyl acetate	100.0	0.185	200–210
Vinyl isobutyl ether	98.7	0.214	230–280
Indene	97.9	0.217	<227
Allyl acetate	64.0	0.288	<240
Styrene	98.8	0.497	275–320

<sup>a</sup> After Reference 45. By permission of Hüthig and Wepf Verlag, Basel, Switzerland.<sup>b</sup> Copolymerizations run under N<sub>2</sub> in dioxane at 70°C, using 1.0 wt. % AIBN initiator.

zation of two complexomers was estimated as 19.7 kcal/mol, with the rate of copolymerization ( $R_p$ ) obeying the following expression:

$$R_p = K[I]^{0.5}[M]^{1.38}$$

If these terpolymerizations do effectively occur by copolymerization of two complexomers, the reactivity constant of each reaction may be estimated in the same fashion as employed in classical copolymerizations. Taking Eqs. (33) and (34) into consideration and the mass law, a copolymer composition expression may be generated, Eq. (38):

$$\frac{m_1}{m_2} = \frac{[D_1]}{[D_2]} \left[ \frac{r_1(K_I/K_{II})[D_1] + [D_2]}{[D_1] + r_2(K_{II}/K_I)[D_2]} \right] \quad (38)$$

where  $r_1K_I/K_{II}$  and  $r_2K_{II}/K_I$  (Table 10.24) are the apparent reactivity ratios of the complexomers  $D_1A_1$  and  $D_2A_1$ .

Using the feed and copolymer composition data and the graphical method of Fineman–Ross,<sup>(516)</sup> it is possible to calculate numerical values for the modified reactivity ratios. Looking at the values in Table 10.24, it is easy to see that the reactivity of the styrene–MA complexomer is usually more reactive than the other charge-transfer complexes. For example, the styrene–MA CTC is about 8 times more reactive than the 2-chloroethyl vinyl ether–MA complexomer.

Examination of a number of the donor<sub>1</sub>–donor<sub>2</sub>–MA polymerizations by this binary complexomer concept has caused some authors<sup>(130,132,149,228,293,527)</sup> to believe that both the kinetics and polymer compositions showed that the chain-propagation reactions were controlled by the charge-transfer complexes. However, the difference in many cases may not be substantial between the copolymerization curves predicted by a complexomer and free-monomer mechanism, since both mechanisms are only considered approximate treatments.<sup>(75,554)</sup>

For the styrene (Sty)–vinyltriethoxysilane (VTES)–MA system, it was pointed out that didonor–acceptor combinations may polymerize via both a CTC–donor and/or CTC–CTC mechanism, depending on the initial monomer feeds.<sup>(402,405)</sup> Studying the Sty–VTES–MA reaction, from both perspectives, it was concluded that the experimental data explained satisfactorily some of the assumptions in copolymerizations involving charge-transfer complexes. However, the data did not provide convincing proof that CTC formation preceded polymerization and whether all of the monomer molecules add to the growing chain in the form of a CTC. Also, the data did not provide the possibility of judging the effect of CTC formation on the overall mechanism of free-radical copolymerization.

Kinetic studies for the Sty–MA CTC with VTES showed linearity at low conversions, with activation energy estimated as 20.7 kcal/mol.<sup>(402)</sup> When the



starting feed ratio was varied to achieve Sty-MA copolymerization with VTES-MA, the activation energy was estimated as being 26.2 kcal/mol. The higher activation energy for the second system was ascribed to polymerization of the two charge-transfer complexes in the latter system. In both cases the rate of copolymerization ( $R_p$ ) increases as the initial concentration of the monomers in benzene increased.

- System 1 (Sty-MA)-VTES:  $R_p = k[I][M]^{1.57}$
- System 2 (Sty-MA)-(VTES-MA):  $R_p = k[I]^{0.53}[M]^{2.25}$

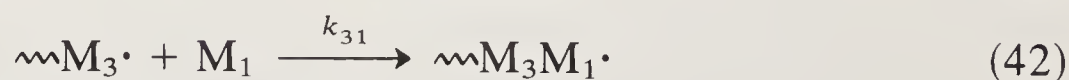
As the acceptor MA concentration is increased, the rate of copolymerization increases and reaches a maximum at 65–70 mol %, but the rate decreases as the content of VTES in the initial mixture is increased. The observed changes in the kinetic parameters suggest that CTC formation between the monomers exerts a substantial effect on the kinetics of ternary copolymerization.<sup>(402)</sup> In addition, the results suggest that copolymerization by both the Sty-MA-VTES and (Sty-MA)-(VTES-MA) charge-transfer complexes occur and theoretical equations of binary copolymerization are applicable to the system.

For the ethylene-vinyl chloride-MA copolymerizations,<sup>(384)</sup> the copolymers contained 50 mol % MA, regardless of monomer feed. The results are consistent with but do not require a mechanism involving copolymerization of charge-transfer complexes.<sup>(384)</sup>

### 10.5.3. Donor-Acceptor<sub>1</sub>-Acceptor<sub>2</sub> Monomer Combinations

Copolymerizations of the monodonor-diacceptor type, where MA is one of the acceptor monomers, have received much less study. 2-Chloroethyl vinyl ether (CEVE)-MA-fumaronitrile (FN) mixtures polymerize to give terpolymers containing 50% CEVE, the donor monomer. This system was examined by both the free propagation and complexomer mechanism concepts.<sup>(552)</sup>

For this particular combination of monomers, treatment by the free propagation mechanism consisting of four different elementary cross-propagating reactions, Eqs. (39)–(42).



where  $M_1$  = CEVE,  $M_2$  = MA, and  $M_3$  = FN.

Assuming steady-state conditions for each active chain, Eqs. (43)–(45) can be considered to represent the composition ratios for the terpolymers.

$$\frac{m_1}{m_2} = 1 + \frac{k_{13}[M_3]}{k_{12}[M_2]} \quad (43)$$

$$\frac{m_1}{m_2} = 1 + \frac{k_{12}[M_2]}{k_{13}[M_1]} \quad (44)$$

$$\frac{m_2}{m_3} = \frac{k_{12}[M_2]}{k_{13}[M_3]} \quad (45)$$

For treatment by the concept of binary polymerization of two complexomers, the following two equilibria [Eqs. (46) and (47)] must be considered.



Assuming copolymerization between  $[M_1M_2]$  and  $[M_1M_3]$  charge-transfer complexes, the Mayo–Lewis<sup>(513)</sup> equation for copolymer composition may be modified to obtain Eq. (48).

$$\frac{m_2}{m_1} = \frac{[M_2]r_1(K_I/K_{II})[M_2] + [M_3]}{[M_3][M_2] + r_2(K_{II}/K_I)[M_3]} \quad (48)$$

Using Eqs. (43)–(45) and the copolymerization results, an average value of 2.73 was calculated for the relative reactivity ratio  $k_{12}/k_{13}$ . This suggests that the CEVE radical reacts with MA about 2.73 times as fast as CEVE radical with FN.

The results of the terpolymerization were also calculated by Eq. (48) and the following modified reactivity ratios obtained.

$$r_1K_I/K_{II} = 2.5 \pm 0.5 \quad \text{for CTC } [M_1M_2]$$

$$r_2K_{II}/K_I = 0.2 \pm 0.2 \quad \text{for CTC } [M_1M_3]$$

Comparing the results from examination of the terpolymerization of CEVE–MA–FN by two different mechanisms, while considering steady-state conditions and possible deviations due to experimental error, it was found that the copolymerizations could well be treated by both methods. In fact, no distinction could be made between the two concepts; i.e., the results neither support nor disprove the CTC mechanism.

The free-radical-initiated copolymerization of the butadiene (BD)–MA–sulfur dioxide (SO<sub>2</sub>) mixture has also been studied as a monodonor–diacceptor system.<sup>(546)</sup> MA is difficult to homopolymerize and SO<sub>2</sub> is not known to



homopolymerize; however, both will undergo free-radical copolymerization with monomers having a small  $e$  value,<sup>(41)</sup> such as styrene and butadiene. Copolymer composition studies showed the BD-MA-SO<sub>2</sub> terpolymers contained 50 mol % of BD, regardless of the starting monomer feed.

Treatment of the system by the free-monomer propagation mechanism gave relative reactivity  $k_{12}/k_{13}$  values of 3.20 at 0°C, 1.34 at 20°C, and 0.95 at 30°C. Using the concept of binary polymerization of two complexomers, the modified reactivity ratios for BD-SO<sub>2</sub> ( $r_1K_I/K_{II}$ ) and BD-MA ( $r_2K_{II}/K_I$ ) were found:

$r_1K_I/K_{II}$	$r_2K_{II}/K_I$	Temperature (°C)
3.0 ± 0.5	0.3 ± 0.3	0
1.2 ± 0.5	0.9 ± 0.3	20
0.9 ± 0.3	1.2 ± 0.5	30

The reactivity of SO<sub>2</sub> is higher than the reactivity of MA at lower temperatures. However, at a temperature slightly less than 30°C, the SO<sub>2</sub> and MA appear to exhibit equal reactivity to BD. In fact, at temperatures above 70°C, due to decreasing reactivity of SO<sub>2</sub>, only BD-MA copolymer is obtained. Since the products of  $r_1r_2$  are close to unit, the copolymerization would seem ideal.

10.5.4. Free Monomer-CTC Mechanism

There appears to be enough experimental evidence to support the concept that in some systems the CTC gets incorporated as such in the alternating polymer chains. However, no experimental phenomena has been presented that would unequivocally show that the CTC plays the decisive role in the polymerization mechanism. Also, it should be remembered that many alternating copolymerizations fail to give perfect 1 : 1 copolymers for all feed compositions, showing that propagation of free monomers also occurs. These and other observations have led several groups to suggest a generalized model for the propagation process of alternating copolymerization, which consists of the reaction of both free monomers and the charge-transfer complexomer.<sup>(20,152,265,427,428,449,558,559)</sup> The work of others support this concept.<sup>(144,162,257,311,406,456,521,526,527,1037,1063,1067)</sup>

The Litt and Seiner<sup>(428b)</sup> kinetic model, which is a combination of both the free monomer and complexomer mechanisms, consists of eight reactions for the possible propagation routes. Pittman and Rounsefelt,<sup>(561)</sup> attempting to further quantify and make general applicability of this concept, have written three computer programs for evaluating the CTC copolymerization model when operating in competition with the terminal (free-monomer) model. Natansohn *et al.*<sup>(1063)</sup> have also explored computer programs for the Litt and



Seiner model. These efforts have demonstrated that no adequate composition-conversion data exist in the literature for adequately testing for a combined CTC-free-monomer model copolymerization.<sup>(561)</sup> This points up the need for much additional work in this area to establish such data if these reactions are to be adequately understood and exploited to make new polymers.

As pointed out, very little has been done on developing a quantitative method for estimating the extent of CTC participating in the propagating step of free-radical alternating copolymerization. Attempting to change this situation, a kinetic method, based on the dependence of the rate of copolymerization upon monomer feed, was recently proposed and evaluated with the vinyl acetate-MA pair.<sup>(429,562)</sup> The method showed the participation of both the CTC and free monomer in the propagating reaction for the vinyl acetate-MA pair.

Using concepts previously discussed in this chapter it is possible to produce new, previously unknown copolymers, with monomers that are easily accessible commercially. Terpolymers with previously unknown properties may be created by terpolymerization of donor-acceptor pairs with neutral monomers, and introduction of reactive groups on these polymers has practical significance. It is obvious that possible applications also include using selected systems or initiators for free-radical, photoreactive, and ionic polymerizations as well as the generation and crosslinking of reactive oligomeric materials. These few mentioned possibilities clearly show that a new field of polymer synthesis reactions is now open, which is of both theoretical and practical interest.

## 10.6. PROPERTIES

With the exception of styrene,  $\alpha$ -olefins, vinyl acetate, and vinyl ethers, little has been published on the physical and chemical properties of alternating MA copolymers, even though there is a wide variety of alternating MA copolymers referred to in the literature. This situation exists mainly because only copolymers made with styrene, ethylene, vinyl acetate, and methyl vinyl ether ever developed substantial market interest. It is estimated that currently about 19 MM lb of MA is being used for the production of all types of copolymers.

### 10.6.1. Styrene Copolymers

Styrene-co-MA resins were first introduced in the 1960s by Sinclair Petrochemicals and called SMA<sup>®</sup> resins. There are two commercial producers of SMA-type copolymers, Monsanto and ARCO Chemical. ARCO's SMA resin series have styrene to MA ratios of 1:1, 2:1, and 3:1, with molecular

weights of 1 600–2 000. The Monsanto resins, which are part of their Lytron<sup>®</sup> series, have molecular weights up to 50,000. ARCO also offers a high-molecular-weight, nonequimolar polymer (see Chapter 9) called Dylark<sup>®</sup>. In addition, American Cyanamid introduced a high-molecular-weight styrene-co-MA polymer as part of their Cypress<sup>®</sup> series. In European and other countries SMA copolymers have often been called Styromol, Maron MS, and Povimal ST resins. Several companies, such as Dow Chemical, Deering-Milliken, and others, captively use SMA-type resins. It is not known which, if any, of these materials are of the 1:1 alternating type. Typical physical properties of two 1:1 SMA copolymers are presented in Table 10.27.

Monsanto’s Lytron resins are marketed as partially esterified styrene-MA copolymers, available as fine, white powders. These resins are insoluble in water, hexane, and toluene, but soluble in bases such as ammonia, sodium hydroxide, potassium hydroxide, and in ketones, alcohols, and ester solvents.

Monsanto also markets a product called Stymer S<sup>®</sup>, which is the sodium salt of a styrene-MA resin. The free-flowing, fine powder picks up moisture readily and is very soluble in water, exhibiting a pH of 7.5–8.5. This product has also been called at various places Sodium Stymer, Vinylite SYHM, Polyco 328, Styromol, and Polvimal resins. SMA resins are easily converted to Stymer

Table 10.27. Properties of 1:1 SMA Resins<sup>a</sup>

	1000	1440 <sup>c</sup>	17352 <sup>c</sup>
Form	White powder	White powder	White powder
Molecular weight	1600	2500	1700
Acid number	480	175	270
Melting range, °C	150–170	55–75	160–170
Bulk density, lb/ft <sup>3</sup>	35	—	—
Viscosity, cSt, at 30°C (10 g/100 ml acetone)	0.67	—	—
Solubility <sup>b</sup>			
petroleum ether	Insoluble	Insoluble	Insoluble
acetone	Soluble	Soluble	Soluble
carbon tetrachloride	Insoluble	Soluble	—
methyl alcohol	Soluble	Soluble	Soluble
benzene	Slightly soluble	Soluble	Soluble
ethylene glycol	Insoluble	Slightly soluble	Slightly soluble
dilute alkaline water	Soluble	Soluble	Soluble
methyl ethyl ketone	Soluble	Soluble	Soluble
ethyl acetate	Soluble	Soluble	Soluble
toluene	Slightly soluble	Soluble	Soluble

<sup>a</sup> From Reference 151.  
<sup>b</sup> 1 g/10 ml solvent (24 h at 25°C).  
<sup>c</sup> Partial esters of the SMA 1000 base resins, with the degree of esterification approximately 35–50%.



S resins by hydrolysis with sodium hydroxide in an alcohol or aqueous medium.<sup>(317,321,322,564,565)</sup> Several articles are available on the properties of SMA-type resins.<sup>(566–575)</sup>

Behavior of styrene-co-MA materials have been studied in solution by light scattering, osmometry, and viscosity.<sup>(569–575)</sup> The resins are brittle, show limited compatibility with other resins, and are insoluble in most common solvents. Ultrasonic absorption and dispersion studies, using pulse-echo techniques, have been investigated in acetone solvent.<sup>(576)</sup> Both as solids and in solution, the copolymer experiences association by intra and intermolecular forces. The degree of association in the solid depends on factors such as the synthesis conditions and thermal history. Association in solution is influenced by solvent polarity, solution age, concentration, and temperature. The association has been attributed to hydrogen bonding between the enol and anhydride form of the succinic anhydride residue.<sup>(574)</sup> The hydrophobic association causes hypercoiling in solution unless the effect is counteracted by electrostatic repulsion from a charged carboxyl residue.<sup>(569)</sup> Systematic investigations of the intrinsic viscosity of SMA resins in acetone, benzene, and xylene shows that in relatively dilute solution the viscosity is directly proportional to monomer concentration during synthesis.<sup>(570)</sup> Above 18 g/100 ml concentration of monomer the intrinsic viscosity becomes proportional to the (peroxide)<sup>1/2</sup>. Particle-size distribution methods have been developed for both the anhydride and derivatives of the copolymer.<sup>(577)</sup>

Ionization, conformational transitions, electrolytic behavior, polysalt formation, etc. of the acid form of the styrene-MA and  $\alpha$ -methylstyrene-MA copolymers have been extensively examined,<sup>(578–590,698,1081,1100,1115,1136,1137)</sup> using potentiometric, dilatometric, and conductometric titration procedures. Colloidal properties of the aqueous salt solutions have also been studied.<sup>(591)</sup> The carboxyl groups on the copolymer are characterized by two intrinsic  $pK_a$  values, where the  $pK_{a2}$  value is 3–5 units greater than the  $pK_{a1}$  value. Linearity of a plot of the ionization of the anhydride copolymer confirmed the systematic transition from a globule to a statistical chain conformation with increased neutralization degree. The anhydride-acid globule form arises from the formation of a hydrophobic core of phenyl groups surrounded by hydrophilic carboxyl group layers. Kinetic studies of the pH-induced conformational transition of the hydrophobic copolyelectrolyte, in aqueous NaCl at ionic strength 0.09, was recently investigated at 25°C by an optical method, using a rapid reaction analyzer at high spectral resolution.<sup>(586)</sup> Plots of the relaxation time against the degree of ionization of the primary carboxyl groups of the acid units agree well with theoretical predictions where the molecule in the compact form is described as a random coil with hydrophobic “pockets.” The Katchalsky-Spitnik equation, adequately describes the situation.

$$pH = pK_a - n \log (1 - \alpha/\alpha) \quad (49)$$



A dye-interactive method is shown to be very useful for determining carboxyl groups in these copolymers.<sup>(592)</sup> At pH < 2, styrene-co-maleic acid precipitates from aqueous solutions. This property can be utilized as a technique to determine the polymer nephelometrically in waste water.<sup>(589)</sup>

The molecular weight of SMA resins is reported<sup>(573)</sup> to be estimated by the following Mark-Houwink relationship:

$$[\eta] = km^2$$

$$[\eta] = 8.69 \times 10^{-5} \bar{M}_n^{0.74} \quad (\text{acetone})$$

$$[\eta] = 5.07 \times 10^{-5} \bar{M}_n^{0.81} \quad (\text{tetrahydrofuran})$$

Others have determined that Flory's  $K_\theta$  values for calculating molecular weights should have the following values<sup>(572)</sup>:

$$K_\theta = 8.8 \times 10^{-4} \quad (\text{acetone})$$

$$K_\theta = 10.1 \times 10^{-4} \quad (\text{tetrahydrofuran})$$

A dual-calibration method for the determination of molecular weights and molecular weight distribution of SMA resins, using gel permeation chromatography (GPC), was recently disclosed.<sup>(593)</sup> A linear relationship of intrinsic viscosity  $[\eta]$  and weight average molecular weight ( $\bar{M}_w$ ) for unfractionated copolymer in tetrahydrofuran at 25°C can be expressed as follows:

$$[\eta] = 3.98 \times 10^{-4} \bar{M}_w^{0.596}$$

The anhydride content of the copolymers examined in the study varied from 5 to 50 mol %, with the  $\bar{M}_w$  range of  $2 \times 10^4$ – $7 \times 10^6$ .

SMA resins swell and eliminate carbon dioxide when heated at 200°C. The resultant soft, brown-colored resins are soluble in acetone, as well as hydrocarbons, to which it imparts a brilliant white fluorescence under ultraviolet light. Pyrolyzed polymer also dissolves in aqueous potassium hydroxide to produce a fluorescent solution.<sup>(594)</sup> Sequence analysis and microstructure of SMA-type resins can be studied by pyrolysis/gas chromatography (PGC).<sup>(595)</sup> Styrene yields are generally extremely low by the PGC technique. In a truly alternating copolymer it might be expected to be zero. For a copolymer showing 51.5 wt. % styrene, the styrene yield was 3.6%.

Dielectric and mechanical measurements have been run on alternating styrene-MA to determine  $\alpha$ ,  $\beta$ , and  $\delta$  relaxations.<sup>(596)</sup> It should be mentioned, SMA copolymers fail to exhibit crystallinity, as shown by x-ray analysis.<sup>(596,597)</sup> Activation energies of each relaxation was estimated. The  $\alpha$  relaxation, attributed to gross chain motion, with  $T_g = 202^\circ\text{C}$ , exhibited very high activation energy. The  $\beta$  relaxation, corresponding to local motion around the backbone of the polymer, exhibited 25.1-kcal/mol activation energy. Deformation of the substituted succinic anhydride rings ( $\delta$  transition) exhibited

activation energy of 12.4 kcal/mol. The transitions agree well with results obtained by differential thermal analysis (DTA) and show the high rigidity of the copolymer structure, which is expected for a five-membered ring unit in the polymer backbone, the copolymer appears to be structurally similar to maleimide homo and copolymers. Torsion pendulum studies tend to confirm these observations.<sup>(596)</sup> Using a volume dilatometric technique, others have estimated  $T_g = 156.3\text{--}157.8^\circ\text{C}$  for the 1:1 copolymer.<sup>(58)</sup>

Attempts have been made to correlate the polymer structures and the electrostatic properties of the SMA-type resins and their derivatives.<sup>(599–601)</sup> Electrostatic charges were measured *in vacuo* after rubbing the samples with iron powder which was attached to a bar magnet. The electrostatic charges of a copolymer composed of two monomers,  $M_1$  and  $M_2$ , which impart charges of opposite sign to the copolymer, depends on the chargeability of  $M_1$  when the content of  $M_1$  is above a certain value, whereas when the content of  $M_2$  increases the chargeability of the copolymer is decided by  $M_2$ . In certain cases the two monomers have the same chargeability with opposite signs and cancel each other. In this case the saturated charges of the copolymers may be estimated from the number of bonds between  $M_1$  and  $M_2$ . This phenomena was observed and studied for both the styrene-co-MA and methyl methacrylate-co-MA materials.<sup>(601)</sup>

Films of 1:1 styrene-co-MA have been examined by the critical angle refractometric method.<sup>(602)</sup> The calculated unit refractivity of  $51.3\text{ ml g}^{-1}$  agreed well with the experimental value of  $50.7\text{ ml g}^{-1}$ . The unit refractivity, which is a product of the specific refractivity and the summation of the atomic weights of the atoms in the polymer units, have been studied.<sup>(603)</sup> The 1:1 copolymer, with a density of 1.286 ( $21^\circ\text{C}$ ), exhibited  $n_D^{21} = 1.564$ .<sup>(603)</sup>

The infrared spectra of various styrene-MA copolymers have been extensively studied.<sup>(604–606,1095)</sup> The absorption bands at 1778, 1720, and  $700\text{ cm}^{-1}$  (KBr pellets) are particularly useful in detecting SMA-type copolymers.<sup>(1140)</sup> Polystyrene exhibits strong infrared absorption bands at 700 and  $759\text{ cm}^{-1}$ . Both these bands are due to out-of-plane deformation of phenyl C-H bonds. The copolymer absorptions at 759 and  $700\text{ cm}^{-1}$  undergo change with sequence length of styrene in the copolymer. The 759/700 absorption ratio decreases from 0.295 to 0.150 on going from pure polystyrene to 1:1 copolymer, providing a good measure of styrene length and copolymer composition. The bands at 858 and  $540\text{--}560\text{ cm}^{-1}$  may also be used to estimate the amount of MA in the copolymer. It is claimed the composition of the copolymer is detected by infrared in solution with an error of  $<2\%$ .<sup>(1095)</sup> For improved accuracy, concentrations of solutions are chosen so that the absorbance is  $>0.1$  for the monosubstituted benzene peak at  $700\text{ cm}^{-1}$  and  $<0.7$  for the MA peak at  $1710\text{ cm}^{-1}$ .

The UV spectra of styrene-MA copolymers have been studied at different monomer ratios over the 254–269 nm absorption range.<sup>(607)</sup> In comparison



with polystyrene, both the position and the absorption coefficient of the bands can depend on the sequence-length distribution of the copolymers, which is believed to be due to dispersion interactions between neighboring phenyl rings.

Chain movement, steric hindrance, and intramolecular interactions of these resins have also been examined by proton and carbon-13 relaxation measurements,<sup>(608)</sup> with the  $^1\text{H}$  and  $^{13}\text{C}$  relaxation times of the styrene units in the 1:1 copolymer considerably shorter than in polystyrene. The data show that the 1:1 SMA copolymer is much more rigid than polystyrene. The  $^{13}\text{C}$ -NMR data also confirms that the microstructure of the copolymer chains can be controlled by varying the monomer composition.<sup>(1145)</sup>

The degree of hydrophilicity and other properties of the copolymers may be changed over a wide range of chemical modifications, such as reaction with alcohols,<sup>(609-617)</sup> ammonia and amines,<sup>(614-624,626,627)</sup> and alkalies,<sup>(322)</sup> giving at the same time numerous useful derivatives.<sup>(628,630)</sup> The mono (*n*-alkyl) amide derivatives may also be modified with potassium or sodium hydroxide to further vary the hydrophilic nature of the copolymers.<sup>(1092)</sup> Reaction of amines, such as aniline, benzylamine, and butylamine, with anhydride containing resins works best in polar solvents.<sup>(1026,1047)</sup> At 60°C, the reaction rates are slightly higher in dimethylsulfoxide than DMF but fails in both cases to exceed 80%. A CTC is formed between the DMF solvent and polymer anhydride rings. It is also known that a CTC forms between styrene monomer and the anhydride groups on a styrene-MA copolymer.<sup>(1046)</sup> Viscometric, conductometric, and potentiometric studies indicate that SMA resins also form 2:1 complexes with polyethylene glycols,<sup>(1020,1139)</sup> where the glycol molecular weight is  $(15-600) \times 10^3$ . Polymeric quaternary ammonium salts have been prepared and studied by reacting SMA with diethylaminoethyl alcohol and quaternization of the polyampholyte with various alkyl halides.<sup>(630)</sup> The polymeric salts, exhibiting typical polyelectrolyte behavior, have been studied extensively.<sup>(1099)</sup> The amino-substituted hydroquinone and  $\alpha$ - or  $\beta$ -aminoanthraquinone derivatives of SMA are water-soluble materials that exhibit unique oxidation-reduction characteristics.<sup>(622,623)</sup> Reactions with benzoin,<sup>(631)</sup> acridine orange,<sup>(632,1115)</sup> mesityl oxide/ $\text{HClO}_4$ ,<sup>(633,843)</sup> *l*-alanine,<sup>(634,635)</sup> and 1,5-diphenyl-3-(3-aminophenyl) verdazyl<sup>(636)</sup> also provide additional understanding of the structure, reactivity of the anhydride and carboxyl groups, and the great worth of the copolymer to prepare unique reactive polymeric materials. Reaction with chiral amino acids (*l*- and *d*-alanine, *l*- and *d*-methionine, etc.) produced chiral copolymers.<sup>(635)</sup> The type of amino acid drastically affected copolymer conformation, ionization, etc., properties.

SMA resins may be chemically modified by a host of other reactions, such as nitration,<sup>(637)</sup> reduction,<sup>(638,639)</sup> chloromethylation,<sup>(640)</sup> sulfonation,<sup>(641,642)</sup> grafting with intermediates such as  $\epsilon$ -caprolactam,<sup>(643)</sup> and treatment with alkyl tin compounds. The latter organometallic copolymers exhibit



attractive biocidal properties.<sup>(644,645,1038)</sup> Lactonization and acylation reactions have also been examined on the copolymers, by using the well-known Perkin<sup>(646)</sup> and Friedel–Crafts<sup>(647)</sup> reaction conditions.

The association and/or chelation properties of both the anhydride and acid form of the copolymer with a great variety of metal ions,<sup>(648,649,652)</sup> metal oxides,<sup>(650–652)</sup> urea and proteins,<sup>(653,654,1030)</sup> clay particles,<sup>(655)</sup> and thiamine disulfide<sup>(656,1031)</sup> have been well investigated. Association of the acid form of the copolymer with poly(*N*-vinylpyrrolidone) has also been studied in aqueous methyl alcohol solutions by viscosity measurements.<sup>(1093)</sup> In 70-vol. % alcohol solution, the viscosity of the mixed polymers solution showed a minimum at the equimolar composition of the carboxyl groups of the styrene copolymer and carboxyl group of the poly(*N*-vinylpyrrolidone), suggesting that polymer-polymer association occurs by a 1 : 1 interaction of the functional groups on the two polymers.

The anhydride and acid copolymer have received some study as interferon inducers and synthetic antigens.<sup>(657,658,1040)</sup>

### 10.6.2. Olefin Copolymers

Ethylene-co-MA resins were first introduced commercially by Monsanto, under the trademark EMA.<sup>(659)</sup> In Europe the copolymers have been called Malethamer and VINAC resins. These copolymers are available in a wide range of molecular weights, in both linear and crosslinked forms. In addition, both the acid form and sodium salt derivatives are also available commercially. Three other olefin-co-MA or acid resins may also be obtained commercially, i.e., octadecene-1 (Gulf Oil Chemicals PA-18), isobutene (ISOBAM by Kuraray Co., Ltd.), and butadiene (Maldene<sup>®</sup> by Borg-Warner Corp.) copolymers. Other  $\alpha$ -olefin copolymers of MA were also offered by Gulf, i.e., PA-6, PA-10, and PA-14, where the numerals designate the number of carbon atoms in the olefin chain. Even though these copolymers were only introduced in 1971, Gulf has since removed them from the market. The properties of these and many other alternating olefin-co-MA resins are briefly reviewed.

A description of some of the typical physical properties of EMA resins are shown in Table 10.28. EMA copolymers are soluble in acetone, pyridine, DMF, and molten MA and insoluble in most of the other common organic solvents. Any free acid is easily removed from the copolymer by standard filter aids.<sup>(660)</sup> The anhydrides react readily to form amides and esters and these materials are soluble in many polar organic solvents.<sup>(659)</sup> Also, the salts of the copolymer are soluble only in water.

The structure and behavior of ethylene-co-MA have been examined extensively. It might be thought that the copolymer, which consists of highly alternating monomer units, would have a crystalline structure. However, electron microscopy and x-ray micrographic studies show the copolymer to

Table 10.28. Properties of EMA Resins<sup>a</sup>

	Anhydride	Acid	Na <sup>+</sup> Salt
Form	White powder	White powder	White powder
Bulk density, lb/ft <sup>3</sup>	20	37	25
True density, g/ml	1.54	—	—
pH (1% aqueous solution)	2.35 <sup>b</sup>	2.35	6
Softening point, °C	170	155	—
Decomposition temperature, °C	247	250	—
Melting point, °C	235	217	—

<sup>a</sup> From Reference 659.<sup>b</sup> Dissolves with hydrolysis to free acid after about 2–3 h at 80°C or 10–15 min at 95°C.

be amorphous.<sup>(661)</sup> Evidently the dimension of the anhydride unit, which exceeds the dimension of the ethylene unit, brings about this condition. However, the polymer does exhibit an endotherm in the DTA at approximately 132–140°C, suggesting some possible crystalline nature in the copolymer.<sup>(662)</sup> At 280°C, the copolymer exhibits about a 10% weight loss and degrades rapidly at about 420–440°C.

The anhydride group in the copolymer may be detected both from the extinction coefficient of the characteristic IR absorption bands of the copolymer and conductometric titration techniques.<sup>(663)</sup> The principal bands in the IR at 1 860–1 780 cm<sup>-1</sup> (C=O in cyclic anhydride), 1 230 cm<sup>-1</sup> (C=O in anhydride), 2 960 and 2 910 cm<sup>-1</sup> (CH<sub>3</sub> and CH<sub>2</sub>) stretching vibrations, and 1 460 and 1 370 cm<sup>-1</sup> (CH<sub>2</sub> deformations) support the alternating structure.<sup>(664)</sup> In some cases a weak absorption band at 725 cm<sup>-1</sup> might suggest a skeletal vibration for –CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>– residues, but little of this sequence could be present. The anhydride residue may also be detected by a common acid–base titration technique, but distinction between free carboxyl residues is not possible.

The Christansen effect, i.e., coloring of MA copolymer dispersions in benzene, has been examined by measuring the temperature dependence of extinction, and the refractive index dependence on frequency and solvent.<sup>(665)</sup> The results were discussed in terms of Christiansen filter effects.

Analogous to the case for the alternating styrene copolymer, the carboxyl groups of the alternating ethylene–MA copolymer exhibits two intrinsic pK<sub>a</sub> values,<sup>(584,587,666,667,1081)</sup> with both larger than succinic acid.<sup>(668)</sup> The UV spectra of partially ionized, hydrolyzed EMA copolymers show that strong H-bonding is not significant.<sup>(1142)</sup> The dielectric properties of the acid form of the ethylene–MA copolymer, in salt-free aqueous solutions, have been found to be analogous to that of ordinary polyacids.<sup>(669)</sup> Controlled hydrolysis techniques are available for obtaining copolymer with 30–80% anhydride content.<sup>(670)</sup>



High-resolution pulsed  $^{13}\text{C}$  NMR studies have been run on the ethylene-co-maleic anhydride polymer polyelectrolyte.<sup>(319,671)</sup> Fourier transforms of the noise-decoupled  $^{13}\text{C}$  NMR free-induction decays were obtained. Titration of the polyelectrolytes can be followed by the changing chemical shifts of the carboxyl carbons. At extremely low pH, only a single major line is observed for the copolymer. At higher pH, the carboxyl carbon line is split into two lines about 0.15 ppm apart. This pattern is maintained even at pH values as high as 11. The separation of the lines is unaffected by the addition of salts to the solution and only slightly reduced by addition of methyl alcohol. The two copolymer lines are assigned to iso and syndiotactic placement of adjacent carboxyl groups with longer-range effects not observable because of the intervening ethylene units. The two tactic placements are present in equal concentrations because of the apparent absence of any selectivity when the MA units in the chain are hydrolyzed to form the polyelectrolyte.

The thermodynamics of the ethylene-maleic acid copolymer aqueous solutions and the counterion binding properties of the polycarboxylates have been thoroughly studied.<sup>(668,672-675,702)</sup> The formation constants for the  $\text{Mn(II)}$ ,  $\text{Co(II)}$ ,  $\text{Ni(II)}$ ,  $\text{Cu(II)}$ ,  $\text{Zn(II)}$ , and  $\text{Cd(II)}$  complexes were measured.<sup>(668)</sup> Calorimetric and dilatometric measurements were used to detect the changes in enthalpy, free energy, and volume in the binding of the  $\text{Ni(II)}$  and  $\text{Ba(II)}$  ions in  $(\text{CH}_3)_4\text{NClO}_4$  aqueous solutions at  $25^\circ\text{C}$  and with different degrees of neutralization.<sup>(672,673)</sup> Volume changes associated with hydrogen and magnesium ion bindings to anions of hydrolyzed polymer showed cooperative H binding to adjacent carboxyl residues. The absorption spectra showed that  $\text{Cu(II)}$  ions were always tightly bound, giving charge-transfer complexes, whereas  $\text{Ni(II)}$  and  $\text{Ba(II)}$  interactions with the copolymer were weak.<sup>(674)</sup> Ag-ion binding was cooperative, as shown by potentiometry, dilatometry, and viscometry. The volume increases with Ag binding, depressing the intrinsic viscosity. The Ag-carboxylate cluster are probably predominately intramolecular.<sup>(702)</sup>

Auramine O and ethidium bromide interactions with hypercoiling olefin maleic acid copolymers have been used as probes to study the polyelectrolyte conformations.<sup>(1096)</sup> The two cationic dyes responded in fluorescence or in visible spectra to changes in conformation of aqueous solutions of maleic acid copolymers with ethylene, isobutene, 2-methyl-1-pentene, or 2,4,4-trimethyl-1-pentene. The fraction of bound auramine is very sensitive to the presence of polyelectrolyte compact coils and to changes in ionic strength and type of counterions. The fluorescence spectra of the ethidium bromide systems also depended on the structure of the compact coils. Dye properties are correlated with the viscosity and equilibrium thermodynamic data for the various copolymers.

In the same manner as the SMA resins, ethylene-co-MA polymers may be dissolved and heated in refluxing alcohols to form clear solutions of the



half-esters.<sup>(613)</sup> Monoesterification is a second-order, reversible reaction.<sup>(676)</sup> Rate constants and thermodynamic functions of activation have been estimated in every case so as to discuss the influence of substitution degree and stereoisomerism of anhydride ring, type of alcohol, reagent, temperature, and solvent effect upon both rate of mono and diesterification.<sup>(1019)</sup> It is also very hard to completely esterify the copolymers. In general, the esterification degree and reaction rate decrease with the alcohol chain length. For the butyl alcohols the esterification rates followed the order *tert*-butylalcohol  $\ll$  *sec*-butylalcohol  $<$  *n*-butylalcohol. Methods have been discovered for complete esterification.<sup>(613,678)</sup> The completely esterified polymer is equivalent to a head-to-head poly(alkyl) acrylate.<sup>(520)</sup>

Studies show that the anhydride copolymer crosslinked with polyols is thermally reversible.<sup>(679,1141)</sup> The reversibility of the crosslinking reaction was monitored by IR, by studying variations of the polymer melt index as a function of temperature (160–250°C). This chemistry should be useful for preparing thermosetting resins, which may be fabricated at temperatures above reversibility of the ester bond formation. Thermosets of this type should also be recyclable.

The EMA anhydride resins may be treated with *N,N*-dialkylaminoalcohols to produce polyampholytes, ammonia, and primary or secondary amines to produce amides and a host of other mono and polyfunctional active hydrogen compounds to produce a wide variety of derivatives.<sup>(621,680)</sup> The primary amine derivatives, i.e., amide–ammonium salts, may be transformed with heat to imide copolymers.<sup>(626,1047,1114)</sup> Surface tension studies have been explored on EMA resins and octadecylamine derivatives of the copolymer.<sup>(681)</sup> The effect of steric hindrance on accessibility, inhomogeneous consideration, electrostatic effects, etc., on the reaction of typical aliphatic amines and polymeric amines (polyethylene imine) with propylene–MA copolymer have been recently examined in great detail.<sup>(682,1137)</sup> The complexity of the reaction did not allow complete separation of the many variables.

Guerra and Palla<sup>(1087)</sup> have recently prepared some unique graft copolymers by reacting polystyryl anions (living polymer) with EMA copolymer. This general reaction is being explored to produce new cation-exchange resins.

Gulf's PA-18 is an alternating copolymer of a long-chain  $\alpha$ -olefin with MA, having both hydrophobic and hydrophilic character. Typical properties of low-molecular weight PA-18 are shown in Table 10.29. Copolymer PA-18 has essentially no solubility in water and very limited solubility in ammonium hydroxide, due to the hydrophobic alkyl residue. Milky white, dilute solutions of the copolymer are prepared with aqueous sodium or potassium hydroxide at pH 11.8, exhibiting good stability. Aqueous solutions of PA-18 salts are compatible with moderate concentrations of monovalent ions, but complex and precipitate with most polyvalent ions. Copolymer PA-18 is soluble in a wide variety of organic solvents, including hydrocarbons, chlorinated aro-

Table 10.29. PA-18 Properties<sup>a</sup>

Form	White powder
Molecular weight	50,000
Melting range, °C	110–120
Anhydride equivalent, moles equiv./g	3.10–3.25
Acid number	270–310
Neutralization equivalent, moles equiv./g	4.83–5.53
Anhydride content, wt. %	15–23
Acid content, wt. %	5–10
Specific gravity	0.97
Volatiles, %	<1
Residual monomer	<3
Inherent viscosity <sup>b</sup>	0.10–0.13
Viscosity at 150°C (cP)	20,000
160°C (cP)	8 000
Thermal stability	
at 250°C (wt. loss %)	1
at 300°C (wt. loss %)	3
at 350°C (wt. loss %)	10
at 400°C (wt. loss %)	23

<sup>a</sup> From Reference 196.  
<sup>b</sup> 5.0 g/100 ml methyl isobutyl ketone at 77°F. Copolymer also soluble in hydrocarbons, chlorinated alkanes, esters, and other ketones.

atics, esters, ketones, and ethers. Analogous to the ethylene and styrene copolymers, PA-18 is capable of being extensively modified by reaction with active hydrogen compounds, such as alcohols and amines.<sup>(196)</sup>

Alternating copolymers of butadiene-co-MA (Maldene<sup>®</sup>) and its derivatives have physical characteristics shown in Table 10.30. There are frequent

Table 10.30. Maldene Physical Characteristics<sup>a</sup>

	285 <sup>b</sup>	286 <sup>c</sup>	287 <sup>d</sup>	270 <sup>e</sup>
Bulk density, lb/gal	7.4	9.1	9.1	9.1
kg/liter	0.88	1.09	1.09	1.09
Solids, %	25	25	42	34
Solvent	Acetone	Water	Water	Water
pH	NA	4.5	2.0	10.5
Color	Amber	Straw	Straw	Amber
Acid number (free acid)	700	700	700	700
Brookfield viscosity, cP	12	250	2 500	25,000

<sup>a</sup> From Reference 683.  
<sup>b</sup> Anhydride.  
<sup>c</sup> Partial ammonium salt.  
<sup>d</sup> Free acid.  
<sup>e</sup> Full sodium salt.



literature references to other alternating olefin-MA copolymers, such as propylene, isobutylene, hexenes, and 2-methyl-1-pentene, cyclopentene,<sup>(1127)</sup> with little development activity. The one exception is ISOBAM (isobutene-co-MA), under development by Kuraray.<sup>(684)</sup> For the most part, very little has been reported on the physical and chemical properties of these systems.

Proton resonance measurements have been made on alternating isobutene-co-MA,<sup>(522)</sup> showing the anhydride units have the *threo*-diisotactic and *threo*-diisyndiotactic configuration. Degradative behavior studies, using pyrofield ion mass spectrometry, gas chromatography, and IR techniques, have been accomplished and a degradation mechanism proposed for ISOBAM-type materials.<sup>(686)</sup> Potentiometric titration<sup>(584)</sup> and polypeptide and metal-cation binding properties<sup>(584,673,675)</sup> have also been briefly examined for the isobutene copolymer.

The physical chemistry of the anhydride and acid form of the 1:1 MA-hexene-1 copolymer have received some study, using viscosity, diffusion, and light-scattering measurements in solvents of varying polarities. In addition, the photoluminescence spectra of the copolymer have received some study, using uranyl ( $\text{UO}_2^+$ ) ions at 77 K.<sup>(687)</sup> The acid copolymer takes on the conformation of a nonpermeated flexible Gaussian coil in 2-butanone and dioxane solvents.<sup>(688)</sup> Thermal decomposition of ion containing copolymers have been examined, with increasing amounts of Li, Na, Rb, Cs, Mg, Ca, Fe(II), Pb, Cu, Mn, and Zn cations, by plotting the weight loss kinetic curves under isothermal conditions.<sup>(689)</sup> Both the thermal and thermo-oxidative stability of the ion containing copolymers increased with increasing degree of neutralization, reaching a maximum at 100% substitution. The stability also increased with increasing ionic radius. An increase in ion concentration increased the thermal stability of the copolymers sharply.

Films of  $\text{C}_{4-10}$  1,1-dialkyl substituted-co-MA copolymers have been orientated by stretching.<sup>(690)</sup> Stretching could be achieved in one direction or in two mutually perpendicular directions in the plane of the film at 150–200°C and draw ratio of 8:1. Uniaxially oriented films have tensile break strength, in the orientation direction, of at least 10,000 lb/in<sup>2</sup>. Biaxially oriented films exhibited tensile strength in any direction in the plane of the film of at least 10,000 lb/in<sup>2</sup>.

Hydrolysis of the 1:1 copolymer of 2,4,4-trimethyl-1-pentene-co-MA has been studied in the presence of Na, K, and Li salts.<sup>(691)</sup> It was shown that hydrolysis resulted in significant interaction between the nearest-neighbor carboxyl residues. At low pH, the polymer was highly coiled. Salts of the copolymer had an expanded conformation over the amide alkaline pH range. This behavior, and the structural flexibility characteristics of the side chains were correlated with the acid-salt dispersant ability. The described interaction is of a type generally observed during the hydrolysis of all 1:1 copolymers of MA.



10.6.3. Vinyl Ether Copolymers

The most important member of this family of copolymers, the 1:1 copolymer of methyl vinyl ether and MA, is marketed under the trademark Gantrez AN by the GAF Corporation. In Europe, Imperial Chemical Industries markets the copolymer as Viscofres. GAF offers the anhydride copolymer in several grades (AN-119, 139, 149, and 169), along with the half-ester (ES resins) and half-amide copolymers.<sup>(692,693)</sup> The general properties of Gantrez AN resins are shown in Table 10.31.<sup>(692)</sup> In marked contrast to SMA and EMA copolymers, Gantrez AN resins are known to have good compatibility with a wide variety of other polymeric materials.<sup>(1082–1084)</sup>

Gantrez AN resins are soluble in ketones, esters,  $\gamma$ -butyrolactone, *N*-methylpyrrolidone, pyridine, and acetic acid. They are insoluble in aliphatic and aromatic hydrocarbons, chlorinated solvents, diethyl ether, nitroparaffins, and dioxane. As shown in Table 10.31, the resins dissolve readily in hot water to form an acid solution of pH 2 (5–10% solids) and slowly in alcohols at room temperature to give half-esters. At any given concentration, the viscosity of aqueous solutions of Gantrez AN is a log function of the molecular weight of the copolymer. The maximum pourable concentration, at room temperature, ranges from 20% for AN-169 through 28% for AN-139 to 35% for AN-119. At higher concentrations very thick gels are formed. Raising the temperature of the aqueous solutions of the copolymers decreases the viscosity logarithmically, for either the acid or salt form of the copolymer. As shown in Table 10.31, unneutralized aqueous solutions of Gantrez AN resins have relatively low pH values and the pH is essentially independent of the molecular weight of the copolymer. The surface tension of the aqueous solutions of the resins is inversely proportional to the concentration.<sup>(692)</sup> The viscosity of aqueous solutions, on storage, have a tendency to drop slightly, especially when exposed to light. Ultraviolet absorbers retard or eliminate this viscosity drop. The copolymers are soluble over the entire pH range, have stability in both acid and alkaline solutions, and are compatible with many other types

Table 10.31. Gantrez AN Resins<sup>a</sup>

Form	White, fluffy powder
Softening point range, °C	200–225
Glass transition temperature, °C	133 <sup>b</sup>
Specific gravity of film	1.37
Bulk density of powder, lb/Ft <sup>3</sup>	20
pH-5% aqueous solution (free acid)	ca. 2

<sup>a</sup> From Reference 692.  $\eta_{sp}$  0.1–0.5 (AN-119);  $\eta_{sp}$  1.0–1.4 (AN-139);  $\eta_{sp}$  1.5–2.0 (AN-149);  $\eta_{sp}$  2.6–3.5 (AN-169); (1.0 g/100 ml MEK at 25°C).  
<sup>b</sup> Taken from Reference 694. The  $T_g$  values reported for the corresponding monomethyl, -ethyl, -propyl, -*n*-butyl, -*sec*-butyl, -*tert*-butyl, and -cyclohexyl maleate copolymers are, respectively, 110, 105, 53, 40, 68, 58, and 50°C.

of resins. Interest in molecular (DNA) repair has even brought about some studies on the pseudophototropy of the Gantrez AN polymer.<sup>(695)</sup> In pseudophototropy, terminal double bond sequences are formed through UV irradiation or oxidation. This is believed identical to the mechanism for DNA repair.

The hydrolyzed 1:1 methyl vinyl ether-MA copolymer also exhibits a two-step titration curve of pH vs. ml of base, with the  $pK_{a2}$  value about 3 to 5 units greater than the  $pK_{a1}$  value.<sup>(581)</sup> The primary carboxyl group has  $pK_{a1} = 4.65$  and the secondary carboxyl has  $pK_{a2} = 8.70$ . A simple theory for describing the potentiometric titration response of the copolymer was recently developed.<sup>(1081,1115)</sup>

The effects of hydrophobic bonding on the macromolecular structure of a series of hydrolyzed alternating alkyl vinyl ether-MA copolymers has received substantial study.<sup>(696-698,1097,1098,1100,1123)</sup> Gantrez S resins are the hydrolyzed form of Gantrez AN. The aqueous solutions showed a balance between hydrophobic nonpolar side-chain interactions and electrostatic repulsive forces of carboxyl residues. The ethyl vinyl ether copolymer behaves as a normal weak polyacid,<sup>(696)</sup> while the butyl and hexyl ether copolymers exist in a hypercoiled state at low pH and undergo conformation transitions to extended state as the degree of neutralization ( $\alpha$ ) is increased. The range over which the transition occurs is shifted to higher values of  $\alpha$  with increasing side-chain lengths. In fact, copolymers with  $C_8$  and  $C_{10}$  alkyl moieties have a tendency to hypercoil even at a high charge density. Proton titration data were used to discuss possible thermodynamic parameters for the possible transition at various  $\alpha$  values and alkyl side-group lengths. Also, the effects of temperature and ionic strength on these parameters have been examined.<sup>(697)</sup>

Addition of sodium, potassium, calcium, ammonium, etc., bases to aqueous solutions of Gantrez AN resins leads to two viscosity peaks, corresponding to 1 and 2 mole equivalents of base. The interpolymers are precipitated by  $Ca^{2+}$  ions and other heavy, polyvalent metal cations, beyond 0.7 mole equivalents. With ammonium hydroxide, peaks tend to be observed at about 1 and 3 mole equivalents of base. Ionic interactions in aqueous solutions of Gantrez AN polyelectrolytes and polycarboxylates, electrophoretic mobility and viscosity of copolymer salts, counterion binding properties, etc., have received substantial study.<sup>(659,672,700-702,1100)</sup> Aqueous polyelectrolyte salt solutions of the isobutyl vinyl<sup>(698,703,1103)</sup> and ethyl vinyl<sup>(704)</sup> alternating copolymers of MA have also recently received substantial study.

Complex formation in aqueous solution between the maleic acid-methyl vinyl ether copolymer (Gantrez S) and polyethylenimine have been studied by turbidity and conductance measurements.<sup>(1085)</sup> The composition of the complex depended on the pH of the medium. At pH 4.7, the complexation proceeded in 1:1 stoichiometry for polyethylenimine of molecular weight



600–1 900. Others<sup>(1086)</sup> have also been studying complex formation between anionic maleic acid copolymers and cationic copolymers, showing that 1:1 complexes are possible even at considerable differences of the average charge distance of the constituting components if the mobility of the charge centers is sufficient.

Using the Anderson–Seddington capillary method,<sup>(699)</sup> the self-diffusion coefficients of Gantrez AN polyelectrolytes and polycarboxylates were detected in the presence of  $\text{Na}^+$  ions. The electrophoretic mobility of aqueous solutions of Gantrez AN sodium salt, in acetic acid–sodium acetate at 25°C with buffers at pH 3.2–10 and extrapolation to zero polymer concentration, showed the intrinsic viscosity of the polymer passes through a maximum value at pH 7.5. In addition to the potentiometric titration procedure, an optical probe method has been used to study acid–base equilibrium properties of Gantrez AN resins.<sup>(705)</sup> Both the titration data and absorption spectra of hydrolyzed 1:1 methyl vinyl ether–co–MA reaction product with 5-(dimethylamino)-*N*-(2-aminoethyl)-1-naphthalenesulfonamide showed that the apparent  $\text{p}K_a$  values for its dicarboxylate groups and of the dimethylamino residues maintained a small constant difference as they increased with increasing degree of dissociation ( $\alpha$ ). In contrast, studies on the dansylated alternating isobutyl vinyl ether copolymer showed both  $\text{p}K_a$  values passed through a maximum as the macromolecule underwent a transition from a compact to a random coil conformation. Clearly, the fluorescence probe method was shown useful for monitoring the conformational transitions from compact hypercoil to random coil for the butyl vinyl ether and other alkyl vinyl ether copolymers of MA.<sup>(706)</sup>

Proton NMR studies of the  $\text{D}_2\text{O}$  hydrolyzed *n*-butyl vinyl ether copolymer have been investigated.<sup>(707)</sup> A sharp decrease in the linewidths of side-chain resonances was noted at a neutralization degree of approximately 0.2. This is the same region where potentiometric titrations show a conformational transition to occur. A similar effect was not noted for the methyl vinyl ether copolymer.

The morphology of methyl, ethyl, cetyl, decyl, and isobutyl copolymers hydrophilic–hydrophobic sequence has been studied and compared in THF and dimethylsulfoxide solvents, using viscosity and light-scattering techniques.<sup>(708,709)</sup> The macromolecular chains have a segregated conformation, which allows the solvent to solvate compatible segments of the copolymer. The unperturbed molecular dimension of the isobutyl vinyl ether–MA copolymer are smaller than that for poly(isobutyl vinyl ether), as shown by the Stockmayer–Fixman equation.<sup>(73)</sup>

Aqueous solutions of hydrolyzed hexyl vinyl and octyl vinyl ether–MA copolymers become turbid with increased pH, even in the presence of  $\text{NaCl}$ <sup>(710)</sup>; whereas water solution of weak polyacids usually increase with increasing pH. Similar results were noted with addition of  $\text{LiCl}$ .



Wide-angle x-ray diffraction studies of hexadecyl vinyl ether-co-MA aqueous gels have been investigated, as a function of water content, degree of neutralization, and temperature.<sup>(711)</sup> A lamellar structure was observed at low degree of neutralization and a cylindrical structure at high degrees of neutralization. This sounds like the copolymer exhibits liquid crystalline behavior. Using copolymer of molecular weight  $(6.3-60.2) \times 10^4$ , variations of structure have been examined for aqueous solutions of the potassium salt.<sup>(906)</sup>

Analogous to the styrene and olefin copolymers, alkyl vinyl ether copolymers may be treated with ammonia<sup>(619)</sup> amines and alcohols<sup>(613,694)</sup> to obtain a large number of derivatives. Properties of these derivatives will not be discussed here but will be touched on briefly under the application section.

The 1:1 *tert*-butyl vinyl ether-MA copolymer undergoes a unique acid-catalyzed rearrangement reaction, using catalysts such as  $\text{BF}_3(\text{OC}_2\text{H}_5)_2$  and  $\text{H}_2\text{SO}_4$  in refluxing alcohols, benzene, and chloroform. The same rearrangement also occurs in the solid phase at  $180^\circ\text{C}$  to give both a poly(carboxylactone) and isobutene.<sup>(74)</sup>

The relative tendencies of Gantrez AN type resins to form complexes with clay materials and other inorganics has received some study.<sup>(712)</sup> Also, the properties of thiamine disulfide complex with ethyl vinyl ether-MA copolymer have been investigated.<sup>(656)</sup>

Methyl vinyl ether-MA copolymer has the property of inducing interferon production in animals, which is potentially useful for inhibiting the growth of Friend leukemia virus.<sup>(657)</sup> The 2:1 divinyl ether-co-MA polyanion cyclopolymer, often referred to as PYRAN, has had extensive study, because of its antitumor and interferon inducer properties. Many structural modifications and derivatives of this copolymer also exhibit antitumor activity, interferon inducing capacity, and a wide spectrum of biological activity. Recent publications<sup>(122-124,713-717,1089-1091)</sup> give adequate coverage of the properties of this very unique copolymer, which is easily crosslinked with divinylbenzene to obtain interesting hydrophilic gels.<sup>(1088)</sup>

#### 10.6.4. Vinyl Ester Copolymers

Commercial products based on vinyl acetate-MA copolymers were until recently marketed by Monsanto under the trademark Lytron 897, 898, and 899. These materials, having a high carboxyl content, exhibit solubility in water and other polar solvents. In addition, Monsanto markets "Benex," Amoco produces Drilling Aid 420 and 421, and Baroid (National Lead) markets "Xtend" vinyl acetate-MA copolymers for oil field applications. In Europe these copolymers have been called "Povimalya" resins. This interest has caused some to give attention to studying the properties of alternating vinyl acetate-MA copolymers.

Tensile strength and elongation properties of the vinyl acetate copolymer have been briefly examined.<sup>(147,718)</sup> The glass transition temperature ( $T_g$ ) was determined to be 100–104°C, by using a volume dilatometric procedure.<sup>(598)</sup> The amorphous, hygroscopic copolymer is soluble in alkali, water, alcohols, acetone, THF, and DMF.<sup>(719)</sup> Paper chromatographic methods have been used to study solvent action on the copolymer.<sup>(721)</sup> The kinetics of hydration in acetone have about the same characteristics as that of succinic anhydride.<sup>(720)</sup> The effects of heating aqueous solutions of the copolymer at 100°C, change of pH on viscosity, surface tension, and foaming properties have been explored and correlated.<sup>(722)</sup> The foaming properties are maximum at pH 4. Introduction of neutral electrolytes such as NaCl, MgCl<sub>2</sub>, and Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> reduced the copolymer viscosity.

Hydrolysis of vinyl acetate–MA copolymer produces a material with lactone rings and carboxyl residues, as shown by IR spectroscopy and other techniques.<sup>(629,723,724)</sup> Esterification, with a reaction order of 2, has been studied for a variety of alcohols.<sup>(1019)</sup> In general, both rates and esterification degree decrease with alcohol length, with Lytron resins esterifying easier than EMA resins. Treating the head-to-head polymer with an acid–alcohol mixture gives products characterized as ester–lactone polymers.<sup>(725,727)</sup> The alcohol attacks the anhydride to give a half-ester. The vinyl acetate was hydrolyzed to the corresponding alcohol, which then reacted with the neighboring free carboxyl group to form a lactone. Also, transesterification can occur to give the lactone ring. None of these reactions goes to completion, as shown by various analytical procedures.<sup>(142)</sup> Mixed ester–lactones are also easily obtained by heating the copolymer in dioxane with hydroxyacids and alcohols. Using <sup>14</sup>C-labeled MA–vinyl acetate copolymers, containing 6–54% anhydride, a semimicro method has been developed to determine copolymer anhydride content.<sup>(728)</sup> The method avoids hydrolysis of the acetoxy residues.

The dilute solution properties of the vinyl acetate–MA copolymer have been examined and the electrochemical, rheological, steric factors, etc., discussed.<sup>(727,729,730)</sup> The unperturbed dimensions of the copolymer are smaller than poly(vinyl acetate), which may be due to strong dipole interactions between the anhydride moieties. Saponification, titration studies, and evaluation of the copolymer as a polyelectrolyte have received some additional attention.<sup>(730,731)</sup> The titration curves and other data suggest that the local charge density dominates the behavior of the copolymer and is very important for the ion-binding properties. The anhydride copolymer is reported to readily form charge-transfer complexes with tertiary amines in acetone solvent.<sup>(732)</sup> The properties of the alternating polyampholyte obtained from the alternating copolymer of MA with vinyl palmitate have been recently studied.<sup>(733)</sup> The change of electrostatic free energy of the polymer solutions, induced by the actual degree of ionization, were detected.



The thermal properties of the vinyl acetate-MA copolymer have been examined both in air and nitrogen over the range 150–200°C.<sup>(144,734)</sup> The copolymer starts to decompose at 150°C and lose acetic acid. Assuming a first-order reaction with respect to weight loss, the activation energy was 542.6 kcal/mol in N<sub>2</sub> and 28.4 kcal/mol in air. Analysis of the decomposed copolymer shows that both double bonds and crosslinks are formed more easily in N<sub>2</sub> than in air, while epoxy residues are formed in air. A mechanism is proposed to account for the various decomposition modes.<sup>(734)</sup> The specific viscosity of the copolymer also decreases with time in DMF.<sup>(735)</sup> Osmotic pressure measurements show chain scission occurs and acetic acid is released when the solution is heated at 100°C. No decrease of specific viscosity is detected when heated in THF solvent.<sup>(735)</sup> The rheological properties of poly(vinyl chloride), polyacrylonitrile, and poly(vinyl acetate) solutions, combined with DMF and 1% vinyl acetate-MA copolymer have been briefly studied.<sup>(727)</sup> In all cases, the viscosity versus composition dependence curves were nonadditive. In addition, the observed deviation was in the direction of a decrease. The magnitude of the deviation from additivity, as a general rule, decreases with an increase in polarity of the homopolymer-copolymer system. Interaction of the homo and copolymer hydrophobic segments were discussed.

Clay complexes<sup>(712,736)</sup> and the binding of copper(II)<sup>(651)</sup> by vinyl acetate-MA resins have received study. Visible absorption, potentiometric titration, and viscosity measurements showed the copolymer strongly binds Cu<sup>2+</sup> ions.

Similar to the SMA system, vinyl acetate-MA may be treated with mesityl oxide and HClO<sub>4</sub> to prepare copolymer with pendent pyrylium perchlorate residues<sup>(633)</sup> and primary amines to prepare imide materials.<sup>(1047)</sup>

### 10.6.5. Other Copolymers

Alternating copolymers of methacrylic and acrylic acid-MA have had some study.<sup>(737)</sup> Intrinsic viscosities  $[\eta]$ , sedimentation constants ( $S$ ), and viscosity average molecular weights ( $M_v$ ) were examined for 10-fractions of a 1:1 copolymer in various solvents.<sup>(738)</sup> Plots of the logarithms of  $S$  and  $[\eta]$  vs  $M_v$  indicated a deviation from linearity at  $M_v = 5 \times 10^5$ , attributed to possibly some branching. The  $[\eta]$  in various solvents indicates that aqueous 0.2 *N* HCl, propyl alcohol, and acetic acid are poor solvents for the copolymer, in comparison to methyl and ethyl alcohol. Increasing amounts of alcohol addition to 0.002 *N* HCl aqueous solution of the copolymer resulted in the degradation of the globular structure of the alternative methacrylic acid-MA copolymer,<sup>(739)</sup> reflected in a twofold increase of viscosity. An increase in length of the alcohol chain shifted the observed transition to lower concentration of alcohols. The calculated unperturbed dimension of the copolymer in ethyl alcohol, DMF, and dimethylsulfoxide conformed to a typical flexible chain polymer.<sup>(739)</sup>



Photomicrographs have also been used to study the structure of the acrylic acid-MA copolymer in aqueous solution at an increasing degree of dissociation.<sup>(740)</sup> The data show the globular form changes to an extended chain form, with a maximum on the curve at the specific viscosity versus pH of pH 9–10. Addition of ammonia to aqueous solutions of the copolymer gives a stable colloid system, which has properties similar to soap solutions. Copolymer solutions in water-ethanol, saturated with ammonia, also have an opalescent property akin to soap solutions. The turbid liquid mixture, which is stable for extended periods at room temperatures, becomes clear on heating. After cooling, the solution returned to an opalescent mixture. Electron microscopy shows the presence of spherical and elongated particles of colloidal dimensions in the liquid. The liquid mixture was considered a polymeric analog of a soap solution. The colloidal properties of the system are apparently due to the supramolecular structuring of the polymer in solution. The alternating copolymer of acrylic acid-MA also forms a complex with poly(*N*-vinylpyrrolidone), according to an interpretation of recent conductometric, potentiometric, and viscometric data on mixtures of these polymers.<sup>(741)</sup>

The antiviral properties of alternating *N*-vinylpyrrolidone-co-MA have received a fair amount of study.<sup>(731)</sup> The copolymer is known as an interferon inducer.<sup>(742)</sup> A large number of amino acids, such as histamine, atropine, and prednisolone, have been used to modify the copolymer to obtain additional antiviral, antibacterial, antiinflammatory, and hormonal active materials.<sup>(743–748)</sup> The acrylic acid-co-MA polymer has also been modified to obtain antiviral materials.<sup>(749)</sup>

The properties of 1 : 1 copolymers prepared from allyl alcohol and derivatives with MA have been very briefly examined.<sup>(33,45,724,725)</sup> The copolymers are soluble in a variety of organic solvents, including acetone, 2-butanone, ethanol, propanol, DMF, dimethylsulfoxide, THF, pyridine, and dilute ammonia or alkalin solutions. A similar copolymer may be prepared from monoalkyl esters of maleic acid.<sup>(750)</sup> Copolymerization of styrene with monoallyl maleate or fumarate hinders cyclization, due to the highly reactive styrene.<sup>(893)</sup>

## 10.7. APPLICATIONS

Copolymers of styrene-, olefins-, vinyl acetate-, and alkyl vinyl ether-MA were introduced commercially to fill the need for resins of low viscosity, water solubility, and high functionality. The aforesaid properties and other copolymer characteristics made for a wide range of possible uses for these materials. In this review on uses, we make no attempt to completely separate out the current uses from past and potential applications.

### 10.7.1. Styrene Copolymers

Product bulletins and a number of articles or books<sup>(670-676,751-757)</sup> describe some of the uses, market size, etc., for SMA-type resins and derivatives of these materials. Some of the important process patents for preparing SMA-type resins are found in Table A.2. For the most part, the largest market areas for SMA resins are coatings.<sup>(197,758-787)</sup> Primer coatings made from these resins exhibit good adhesion to metals,<sup>(767)</sup> corrosion resistance,<sup>(768)</sup> and effective rust removal for corroded steel plates.<sup>(1105)</sup>

Dispersants prepared from SMA function very well for production of poly(vinyl acetate),<sup>(774-776)</sup> poly(vinyl chloride),<sup>(777,781)</sup> vinyl acetate-vinyl chloride copolymers,<sup>(777)</sup> poly(acrylonitrile),<sup>(779)</sup> and other materials.<sup>(322,778-789,1050)</sup> ARCO claims that the SMA 1440 copolymer has exceptional capability to disperse  $\text{TiO}_2$  in latex paint formulations.<sup>(751)</sup> The ammonium salt of the copolymer half-esters also looks attractive as a pigment dispersant for coatings<sup>(790)</sup> and a pigment fixation agent for textiles.<sup>(318)</sup> In addition, the resins show possible utility as electrodeposition-type coatings<sup>(791-793)</sup> and enteric coatings for medicinals.<sup>(794-796)</sup> SMA resins have also been approved for packaging materials that come in contact with food.<sup>(797)</sup> The amidated, ammonium salt of SMA is also cleared under the FDA cosmetic act as a surface sizer in paper or paperboard substrates having possible contact with food.<sup>(797)</sup> Carpet shampoos, where the resin functions both as a dispersant and embrittling agent, are valuable uses of the resins.<sup>(802,803)</sup>

Thermosetting resins and composites prepared from combinations of SMA resins with epoxy resins have high heat distortion, good water and solvent resistance and other attractive features.<sup>(804-806,1107)</sup> SMA resins and derivatives of these materials function well to improve the bonding strength between glass fibers, Kaolin clay, talc, shell,  $\text{ZnO}$ , calcium silicate, etc., fillers and various thermoplastics.<sup>(807-809)</sup> This bonding strength is uniquely demonstrated in a recent patent, where aqueous solutions of SMA are claimed to be useful as sand binder for foundry applications.<sup>(1030)</sup> Polyolefin-metal adhesion may also be promoted by SMA. Composites prepared from sawdust and SMA resins show good moisture resistance and have potential plastics applications.<sup>(810-812)</sup> Biodegradable plastics have been prepared from SMA resins. Also, biodegradable and water degradable fibers may be prepared from SMA-poly(vinyl acetate) polyblends.<sup>(1080)</sup> Crosslinked SMA resins are useful for modifying polypropylene to improve dyeability and modification of injection-molded polystyrene to prevent electrostatic charge.<sup>(813,814)</sup>

SMA copolymers have received study and been shown useful as resin substitutes for paper sizing,<sup>(815-818,1109)</sup> binders for printing dyes,<sup>(819)</sup> barrier resins for electrofax paper and offset printing paper,<sup>(820)</sup> modifier for lithographic printing plate solutions,<sup>(821)</sup> and binders for water-based ink compositions.



Textile warp sizing resins, soil release agents, and such, may be made from SMA resins.<sup>(316,317,323,822-826,1106)</sup> Intermediate sizing of this type removes static charge and improves fiber adherence and resistance to wear. The yarn is protected during weaving and productivity is improved. It was reported that these Styromal-type resins are nontoxic to humans.<sup>(827)</sup> Salts of the SMA resins have the unique property of being useful to prepare textile coatings that are resistant to various gas penetration. The resins can function as dye carrier materials for textiles. Poly(acrylonitrile) fibers prepared in the presence of alternating SMA resins have improved properties. Carbon fibers treated with SMA resins give composites with improved properties, due to adhesion improvement between the fibers and various resins.<sup>(828)</sup>

SMA resins and derivatives of these resins have properties useful in leather processing<sup>(829,830,832)</sup> and adhesives for leather and textiles.<sup>(833)</sup> In the photographic film field, SMA resins are useful for modification of gelatin mixtures, a basic mordant dye carrier, antihalation layer, and emulsion coagulant coating.<sup>(320,834-836)</sup> Amine derivatives of a variety of alternating MA copolymers, including styrene comonomer, have been used to prepare antistatic additives for fuels, including the metallic salts as diesel fuel additives.<sup>(837)</sup>

Compounds such as cysteamine and naringinase may be covalently bound to SMA giving enzymically active materials. Copolymer with covalently bound naringinase shows the useful property of debittering juices.<sup>(838,839)</sup> The anti-tumor antibiotic compound neocarzinostatin (NCS) has been covalently bound to SMA.<sup>(1025)</sup> The lipophilic NCS derivative exhibited increased chemical and biological stability and appeared to possess similar *in vitro* biological activity. SMA has potential for designing other drug binder systems.<sup>(855)</sup> The reaction of horse, rabbit, sheep, and mice antibodies with SMA has been studied, showing the copolymer is an immunogen and possible polydonal B cell activator.<sup>(1040,1110)</sup>

Imide derivatives of SMA materials may be prepared from ammonia and primary amines.<sup>(626,840,841,1047)</sup> Materials of this nature show possible utility in preparing macroreticular granules for peptide synthesis and halogen carrier applications.<sup>(842)</sup> In addition, several amine derivatives of SMA resins have been shown to be possibly useful as dyes.<sup>(843,844)</sup> SMA maleimides have been converted to *N*-methylol materials. Heating the *N*-methylol polymer causes crosslinking and provides a possible agent for protein separations.<sup>(856)</sup> SMA resin gels are useful as a medium for selenium crystal growth.<sup>(845)</sup>

Photoreactive<sup>(846,847)</sup> and photochromic<sup>(1036)</sup> resins are easily prepared from SMA materials. For example, coupling 4-glycidoxychalcone<sup>(846)</sup> and  $\alpha$ -(4-azidophenoxy) ethanol<sup>(847)</sup> to SMA gives potentially useful photosensitive coatings. Covalently bound 4-aminoazobenzene derivatives are useful in reversible hologram recording materials.<sup>(1094)</sup>



Insoluble polyelectrolytes prepared from SMA resins have been explored for waste water purification. Materials of this nature have been shown to be useful to purify waste water from poly(styrene plants)<sup>(848)</sup> and possible isolation of enterovirus and heavy-metal ions.<sup>(849-852)</sup> In addition, SMA polyelectrolyte resins have been explored for use in coagulation of petroleum emulsions.<sup>(1108)</sup> Membranes prepared from SMA polyelectrolytes<sup>(853,854,1028)</sup> are another potential use for SMA materials. Modified SMA resins have also been explored as binders for battery electrode preparation, in particular a binder for the silver-zinc battery.<sup>(857,858)</sup>

Alternating MA copolymers, including the styrene comonomer, have applications potential as detergent builders.<sup>(859-861)</sup> In many cases, such copolymers improve the sequestering properties of the detergent formulation. SMA-Carbowax<sup>®</sup> 350 (Union Carbide) combinations were shown useful modifiers for poly(vinyl alcohol) and cellulosic ether film packets for laundry detergents.

The patent literature (Table A.2) discloses that combinations of polyhydric alcohols with SMA resins have been explored for generating coatings and molding resins. In addition, the allyl esters of SMA resins are useful for modification of unsaturated polyesters to give coatings. Polyurethane foam intermediates are also readily prepared by esterification of SMA resins. Ester derivatives of SMA may be used to modify Portland cement to increase adhesion to steel, extend the setting time of gypsum plaster, and give low-density plaster compositions.

Reaction products of various long-chain alcohols with SMA resins provide materials to reduce the pour point of shale oil. Also, various long-chain amine derivatives perform as ashless lubricating oil detergents. Such materials may also function as metal cutting fluids.

Reactions of various tin containing compounds, i.e.,  $R_3SnOH$  and  $R_3SnOSnR_3$ , with SMA resins provide polymeric materials with pesticidal and antimicrobial properties,<sup>(324,798-801,1038)</sup> as well as other biological and antifouling activities.<sup>(922)</sup> The tin containing copolymers are claimed to be very useful for marine coatings, to obtain long-term resistance to marine organisms. This is expected, since it has been shown that modification of SMA-type resins via copolymerization of small amounts of trialkyl methacryloxy-stannane also produces biologically active materials.<sup>(923)</sup>

Injection molded Dylark<sup>®</sup>, ARCO's high-molecular-weight, nonalternating styrene-MA copolymer (see Chapter 9) is highly useful in the automotive industry. The product has been used as an automotive crash pad retainer since 1972.<sup>(865)</sup>

Rubber-modified styrene-MA copolymer looks attractive in heat-resistant molding compositions.<sup>(925,926)</sup> Modification with various halogenated materials and antimony oxide produces fire-retardant moldings.

The alternating copolymers of *p*-hydroxystyrene and *p*-isopropenylphenol with MA (Table A.6) have recently received a fair amount of study. These copolymers, with two different types of functional acid groups, are being studied in polyion complexes for membranes, detergent additives, epoxy resin curatives, rubber additives, coatings, adhesives, laminates, ion-exchange resins, and other applications. The equimolar 2-allylphenol and 2-methallylphenol-MA copolymers (Sec. 10.2.1) are potentially useful in many of the same applications.<sup>(46)</sup> Maruzen Oil has announced their intention to produce and test market the *p*-hydroxystyrene copolymer.

### 10.7.2. Olefin Copolymers

Several articles, books, and company product bulletins describe some of the uses, market size, and market projections for olefin-MA resins.<sup>(659,754,757)</sup> It is surprising that these copolymers have only achieved a low annual market volume, in view of the many possible uses claimed for EMA<sup>®</sup> (Monsanto Company), 1-octadecene-MA (Gulf PA-18), isobutene-MA (Kuraray's ISOBAM), butadiene-MA (Borg-Warner's Maldene<sup>®</sup>), and other olefin copolymers claimed in the extensive patent literature (Table A.3).

Water-soluble EMA resins and derivatives of these materials function very well as dispersants (Table A.3). For example, the amide-salt derivative exhibits excellent dispersant properties for pigments in waterborne synthetic latex systems. Dispersants for the coatings, rubber, leather, cosmetic, ceramics, photographic film, and agricultural field have been claimed for EMA resins. The linear derivatives are especially useful as dispersants and stabilizers for emulsion bead polymerizations. For example, EMA-type dispersants (emulsifiers) are very useful for PVC production. The resins also function well as macromolecular dispersants for the suspension copolymerization of  $\alpha$ -olefins and aromatic vinyl compounds with MA.<sup>(197)</sup>

Derivatives of EMA resins show very useful properties as thickeners, stabilizers, suspending agents and so forth, for detergent applications.<sup>(859-864)</sup> The *n*-dodecylamide derivative, for example, is an excellent suspending agent for hydrophilic substances and a stabilizer for sodium perborate.<sup>(864)</sup> The physicochemical properties of EMA as a detergent builder and the detergency properties of the EMA resins have been studied and compared to sodium tripolyphosphate.<sup>(861)</sup>

Ester, amide, and other derivatives of EMA and blends of EMA with other resins are claimed to be useful as adhesives (Table A.3). It is known that the acid form of the copolymer is an excellent adhesive for bonding polyolefins to a variety of substrates. The copolymer also functions well as an antislip adhesive for polyethylene bags. Crosslinked EMA resins are potentially useful as thickeners and tackifiers for solution and emulsion



adhesive formulations.<sup>(1141)</sup> Combinations of EMA resins with dextrin, starch, poly(vinyl acetate), animal glues, and synthetic rubber emulsions are claimed in the patent literature (Table A.3) to give improved adhesives for high-moisture-content lumber.

Paper and textile sizing agents may be made from EMA resins.<sup>(1077)</sup> In paper applications, the resins modify the viscosity of latices for sizing and enhance the ink holdout characteristics of the size. The resin also functions well as a thickener for textile sizing latices. Warp sizing agents for polyester and nylon fiber or yarn may also be prepared from EMA resins.

Table A.3 shows that EMA resins and its derivatives are also claimed to be useful in many other applications. Such uses include thickeners for other polymeric systems, shampoos, paint removers, and latex binder for nonwoven fabrics. Derivatives of the resins function well as suspending agents for fillers and powdered chemicals such as insecticides, cleaning solutions, lubricants, ceramics, and other applications. The diisobutylene-MA sodium salt material has been cleared for use as a dispensing or suspending agent for pesticide delivery systems.<sup>(891)</sup>

Derivatives of EMA resins are useful in both the oil field and as additives for fuel oils or lubricants. As additives for oil well drilling muds, the derivatives help reduce water loss due to filtration and perform as viscosity control agents. Long-chain alkyl amine derivatives are useful as antistatic additives for fuel oils.<sup>(837)</sup> Antistatic coatings are also readily available for many other applications. Aqueous solutions of EMA resins are claimed to be useful in foam systems for dust control. For example, aqueous solutions of the resins can be used to trap 90–95% of the airborne dust generated in a coal cutting laboratory.<sup>(866)</sup>

Crosslinked EMA resins have been examined as ion-exchange resins. Special derivatives of these resins show utility for peptide synthesis,<sup>(867)</sup> thiol recovery systems,<sup>(868)</sup> and resins for concentrating virus from sewage.<sup>(869,870)</sup> Immunosorbents with high capacity to isolate antibodies or antigens may be prepared from EMA resins.<sup>(871–873)</sup> Various enzymes have also been covalently bonded to EMA to provide highly useful immobilized enzymes.<sup>(670,839,874–881)</sup> In most cases the immobilized enzymes exhibit enhanced temperature and lyophilization stabilities, along with enhanced stability to alkaline pH and cationic resin stability in acid pH. These enzyme modified resins are potentially useful for isolating histocompatible antigens present on cell membrane surfaces. Enzymes, such as trypsin, pronase, and pepsin, have been linked to the resins. Trypsin-coupled materials are potentially very useful for isolating protein, hexoamines, sialic acid, and other chemicals from tumor cells. A recent patent<sup>(1039)</sup> claims alkoxy-alkylamine derivatives of EMA give a polyelectrolyte useful for isolation of Factor VIII clotting factor from human blood.

EMA resins and esters of these materials have received some attention as enteric coatings or slow-release coatings for medicinals.<sup>(882,883)</sup> The ester



derivatives look very useful for sustained release coatings. Both linear and crosslinked EMA (Malethamer) resins have been studied and shown useful to combat viral infections in animals.<sup>(884–889)</sup> The carboxylate (polyanion) materials inhibit tumor growth and infections in animals when present during inoculation. The crosslinked copolymer (Malethamer) functioned as an agent to detoxify staphylococcus aureus S<sub>6</sub> or clostridium botulinum enterotoxins in monkeys. Injection of EMA resin in tobacco leaves resulted in induced resistance which developed gradually after application, to both lesion number and size during viral infection.<sup>(888)</sup>

Isobutylene–MA copolymers (ISOBAM) are potentially useful raw materials for preparing adhesives,<sup>(892)</sup> paints, and sizing agents<sup>(894)</sup> for paper or fibers.<sup>(684)</sup> A recent review describes the manufacture of plywoods with  $\alpha$ -olefin–MA copolymers, in particular ISOBAM polymer.<sup>(1027)</sup> By analogy to SMA and EMA resins, ISOBAM copolymers are also highly effective dispersants. For example, ammonia derivatives of ISOBAM are very efficient for inhibiting calcium carbonate precipitation from aqueous solutions.<sup>(895)</sup> In agriculture, this copolymer is very effective to bind silt or loam soils.<sup>(896)</sup> As shown in Table A.3, these copolymers also have many other potential applications.

Table A.3 shows long-chain  $\alpha$ -olefin–MA copolymers are potentially useful for preparing oil additives, wax extenders for paper, sizing agents for paper and textiles, cosmetics dispersants, and many other applications. Gulf's product literature on PA-18 points out that modification of the anhydride residue with aqueous bases, ammonia, amines, alcohols, and epoxides may provide a host of potentially useful products.<sup>(196)</sup>

Copolymers of propylene and hexene with MA, as shown in Table A.3, are also useful for preparing many products. Thermosetting resins prepared from the 1-hexene copolymer and epoxy resins may be fabricated into laminates with high heat distortion, good solvent resistance, and other attractive properties.<sup>(805)</sup> Wood composites made with the same blend of alternating copolymer and epoxy resins are also potentially highly useful wood–plastics.<sup>(897)</sup> Propylene–MA copolymers show great utility to prepare blends and laminates from polyolefin–nylon combinations.<sup>(898)</sup>

Nippon Zeon has explored uses for the cyclopentene–maleic acid copolymer.<sup>(1104)</sup> The copolymer is useful as a water-reducing agent for a high-strength concrete mixture.

As pointed out earlier, Borg–Warner markets copolymers of butadiene–MA under the name Maldene<sup>®</sup> resins.<sup>(683)</sup> Table A.3 shows the butadiene and isoprene copolymers have been claimed to be useful for coatings, surfactants, sealants, adhesives, tackifier, binder, paper and textile sizing, quenching agent for metals, and molding and laminating resin applications. The laminates prepared from blends of the butadiene copolymer and styrene show attractive dielectric and mechanical properties.<sup>(899)</sup> Carbon fibers treated with the

isoprene-MA copolymer and used to prepare laminates with epoxy resins show improved shear strength, impact resistance, water resistance, and other features, over some laminates prepared from untreated fibers.<sup>(828)</sup> Borg-Warner is promoting Maldene<sup>®</sup> as a chemical intermediate resin or modifier material for preparing products useful in the textile, adhesives, detergent, and cleaner applications areas.<sup>(683)</sup>

### 10.7.3. Alkyl Vinyl Ether Copolymers

GAF Corporation, as described earlier, markets a series of water-soluble methyl vinyl ether-MA resins called Gantrez<sup>®</sup> AN materials.<sup>(692,693,754-756)</sup> For the most part, these resins find use in adhesives, detergents, textiles, and cosmetics with hair sprays being the single largest use for these resins. Among other numerous uses (Table A.4), the more significant applications include protective colloids and paint-leveling agents. Other areas of possible use include oil-drilling mud additives, pressure-sensitive adhesives, remoistenable label adhesives, microencapsulated paper coatings, denture adhesives, and photosensitive plates, and in textiles as sizing and thickeners for printing materials. The waxy copolymer prepared from octadecyl vinyl ether has been shown to be highly useful as a release coating and antiblock agent.<sup>(692,693)</sup> The high price of these resins has severely restricted their use to specialty markets such as hair sprays and time-release pharmaceuticals.<sup>(1101)</sup> It is estimated that about 5-6 million lb of MA is currently used to manufacture Gantrez AN type resins.

Gantrez AN resins have been suggested as a replacement for sodium tripolyphosphate and other phosphates commonly used as detergent builders.<sup>(758,861,900-904)</sup> The copolymers also function very well as stabilizer additives for heavy-duty liquid detergent formulations and as deflocculants for hard water detergents. As polymeric additives, these resins prevent scale formation or precipitation of alkaline hardness salts from saline waters.<sup>(905)</sup> If such uses could be fully developed, a substantial market for Gantrez resins could be realized. However, lack of biodegradability and economic considerations would appear to preclude this future.

Gantrez resins and other alkyl vinyl ether-MA copolymers, after substantial study, have also been found to be potentially useful as polysoaps,<sup>(906-911,965)</sup> with excellent dispersant strength or emulsifying power. Ester derivatives of the materials function very effectively as polymerization dispersants.<sup>(780,788)</sup> The resins also perform very well as aqueous thickening agents for latex paints and other applications.<sup>(912,913)</sup>

The uses of Gantrez AN resins in cosmetic preparations, such as gels, creams, and aerosol hair sprays, have had extensive examination.<sup>(914-916)</sup> Many derivatives, in particular esters, of the resins also function well in many of these applications.



Table A.4 shows that Gantrez AN resins and derivatives of these copolymers have been claimed to be useful for controlled-release coatings or binders for drugs<sup>(563,796,917–934,1101)</sup> and insecticides.<sup>(935)</sup> The pharmaceutical film coatings show high gloss, clarity, abrasion resistance, flexibility, and other properties with apparently safe use in human consumption. The resins have also had brief examination in ophthalmic applications.<sup>(936)</sup> It is interesting to note that the copolymers apparently help heal animal wounds,<sup>(937)</sup> reduce lead accumulation in animals exposed to lead alkyls,<sup>(938)</sup> and provide other useful immunological properties.<sup>(939)</sup>

A variety of compounds, such as chlorophyll, trypsin, and naringinase, have been covalently coupled to Gantrez resins.<sup>(839,940–943)</sup> The technique provides water-soluble fluorescent pigments<sup>(941)</sup> and immobilized enzymes with increased stability and prolonged activity. Analogous to the SMA resins, the immobilized naringinase materials are highly useful for debittering grapefruit juices.<sup>(839)</sup>

Crosslinked polyelectrolytes prepared from Gantrez resins exhibit the attractive property of being useful for detection of viruses present in natural or sewage water.<sup>(869)</sup> The viruses are absorbed at pH 5.0–6.0, concentrated, and eluted for detection at pH 8.0–9.0.

In the area of hydrophilic membrane chemistry and technology, Gantrez resins and other alkyl vinyl ether–MA copolymers have received substantial study.<sup>(869,944–952)</sup> Ion selective and ion excluding, high  $\text{Na}^+/\text{K}^+$  specificity, and other membranes were examined. Reverse osmosis membranes for desalination of brackish sea water were prepared from poly(*N*-vinylpyrrolidone) complexes with the various alkyl vinyl ether copolymers.<sup>(950)</sup>

A large number of patents (Table A.4) claim oil and lubricant additives prepared from alkyl vinyl ether–MA copolymers. Antistatic fuel additives are readily prepared from the materials.<sup>(837)</sup> Long-chain esters ( $\text{C} > 10$ ) of Gantrez AN show possible use as viscosity index improvers for lube oils.<sup>(954)</sup> The vinyl ether of hydrogenated sperm oil has also been copolymerized with MA to produce a very effective viscosity index improver.<sup>(953)</sup>

Gantrez AN resins and other alkyl vinyl ether–MA copolymers have had extensive examination in paper coatings, textile sizing, leather treatment, and other applications,<sup>(955)</sup> as shown in Table A.4. Durable antistatic coatings for Nylon fibers have been prepared.<sup>(956)</sup> The copolymers have also been examined as binders for explosives<sup>(957)</sup> and modifiers for  $\text{Ag}_2\text{O}$ –Zn cells.<sup>(966)</sup>

Alkyl vinyl ether–MA copolymers have had considerable study in the area of soil conditioners, flocculants for kaolin and montmorillonite clays, chelation of alkaline earth ions, and additives for oil well drilling fluids.<sup>(648,958–961)</sup> The copolymers function well in soil aggregation, to increase crop production.

In photography, Gantrez AN resins and derivatives function as emulsion stabilizers, hardeners for gelatin, antistatic coatings, antihalation coatings, and



subbing layers.<sup>(836)</sup> Electron and photosensitive resins are readily prepared from Gantrez resins. Copolymers with covalently linked stilbene,<sup>(964)</sup> allyl,<sup>(962)</sup> and azido residues<sup>(963)</sup> crosslink rapidly on exposure to light or an electron beam. Technology of this type offers unique procedures for preparing adhesives, coatings, and photoresists.

Many other possible uses are claimed for alkyl vinyl ether-MA copolymers, Table A.4. These uses, calling for the resin to be employed as an additive or modifier or as the main component in a resin mixture, are too numerous to discuss.

The copolymer of divinyl ether-MA (PYRAN) and derivatives of the copolymer have properties potentially useful in a variety of medical applications.<sup>(1120,1121,1124)</sup> Analogous to Gantrez AN resins,<sup>(967)</sup> PYRAN copolymers are interferon inducers, with antiviral activity.<sup>(968-972)</sup> PYRAN inhibits Lewis lung carcinoma growth,<sup>(973)</sup> Friend's leukemia,<sup>(974,975)</sup> lymphoid leukemia,<sup>(976)</sup> foot-and-mouth disease,<sup>(972)</sup> and tumor growth<sup>(977-979,1111)</sup> in animals. The material has also been shown to prolong sleeping time,<sup>(980)</sup> alterate drug metabolism,<sup>(981)</sup> and provide other macrophage activation effects. These antiviral and immunological responses make these copolymers and their derivatives highly interesting.<sup>(982-985)</sup> The 5-fluorouracil derivative of PYRAN was very recently examined and shown to be effective for treating lymphocytic leukemia in animals.<sup>(986)</sup>

#### 10.7.4. Vinyl Ester Copolymers

Monsanto, until recently, produced high-molecular-weight vinyl acetate-MA materials as part of their Lytron resin series. These materials have been investigated as extenders for bentonite mud and as flocculants for drilling clays (Table A.5).<sup>(754,987-989)</sup> The high carboxyl content and water solubility of these materials suggest these copolymers should have many uses in applications requiring dispersants, emulsifiers, and stabilizers. As additives to promote adhesion and coreactants in thermosetting formulations, the copolymer should provide property improvements.<sup>(990)</sup> The patent literature (Table A.5) makes many additional claims of uses for this family of copolymers.

Vinyl acetate-MA copolymers have been called VAMA resins. VAMA and derivatives function well as dispersants for poly(vinyl chloride) production and other emulsion copolymerizations.<sup>(197,731,780)</sup> The copolymer is highly effective for stabilizing other oil-water dispersions.<sup>(992)</sup> The hydrolyzed copolymer, with vinyl alcohol residues, is also very effective for generating fine dispersions of poly(vinyl chloride).<sup>(991)</sup>

VAMA materials function well in detergent,<sup>(861)</sup> boiler scale removal, and chelating applications.<sup>(651)</sup> The copolymer shows excellent chelating properties for  $\text{Cu}^{2+}$  ions. The copolymer may also be used as a coagulating agent for purification of feedwaters going to steam boilers. In this or other

water applications, the copolymer may be detected quantitatively by measuring the extinction at the copolymer wavelength maximum UV light. The minimum concentration for optimum detection is  $8.0 \mu\text{g}/9 \text{ cm}^3$  and the sensitivity of the method, expressed by optical absorption coefficients, was  $3.0 \mu\text{g}/\text{cm}^3$ .<sup>(557)</sup>

VAMA, as shown in table A.5, is claimed to be useful in various adhesive systems. Adhesion of VAMA to cellulosic materials, in terms of structure, polarity, and tack temperature, has been well studied.<sup>(752,993)</sup>

In the agriculture area, VAMA resins are useful for fertilizer coatings and binders and soil modifiers.<sup>(994–996,1102)</sup> The resin stabilizes soil crumb and acts as a soil structure builder to prevent soil erosion.<sup>(712,997–1003)</sup> Crop soils treated with VAMA resins and salt derivatives of the resin have improved quality and as a result of improved bacteria growth and nutrient utilization produce greater yields of various grains.<sup>(1004–1007)</sup>

Table A.5 shows that VAMA-type resins have many other possible uses, such as oil additives, coatings, paper and textile sizes, cosmetics and photographic applications.<sup>(1008)</sup> Polymeric food dyes may be prepared from the resin.<sup>(1009)</sup> This is important when one considers the concern that exists over typical food dye influence on human health and the need to prepare nonmetabolized food dyes.

A terpolymer of vinyl acetate–maleic acid–vinyl chloride looks to be potentially useful for reducing the surface resistivity of chlorinated poly(vinyl chloride).<sup>(1010)</sup> The terpolymer may also be useful in a variety of antistatic coatings.

Table A.6 shows that many other vinyl, allyl, isopropenyl, and other ester copolymers and their derivatives have potential uses as emulsifiers, dispersants, adhesives, coatings, photoreactive resins, aqueous thickeners, oil additives, and others. Allyl acetate–MA copolymer sodium salt is comparable to sodium tripolyphosphate as a detergent builder.<sup>(1011,1012)</sup> In addition, the copolymer provides protection of the fabric against sodium perborate damage.

#### 10.7.5. Miscellaneous Copolymers

Many other monomers have also been copolymerized with MA and the resultant materials claimed to be useful in coatings, adhesives, laminates, dispersants, emulsifiers, oil additives, cation-exchange resins, and other applications (Table A.6). Table A.6 covers patent claims for copolymers prepared from monomers not including styrene, vinyl acetate, and typical  $\alpha$ -olefins or alkyl vinyl ethers.

Low-molecular-weight anionic copolymers prepared from acrylic acid and MA offer potential in many applications requiring dispersants.<sup>(987)</sup> The MA–co–vinyl pyrrolidone copolymer was believed to also exhibit potential use as a dispersant and oil well drilling mud additive. However, the availability



of lignosulfonates and the high cost of these resins works to preclude such uses. Medical applications could develop for this resin, since the copolymers stimulate interferon production and exhibit antiviral properties in animals.<sup>(1013-1017)</sup>

Vinyl silane-MA copolymers and derivatives of these materials have been examined in glass container coatings.<sup>(1018)</sup> The coatings were claimed to protect the annealed glass from physical abrasion and corrosion and preserve the strength of the glass container over the use cycle. Ethylene ionomer type polymer coatings, which are more economically produced, have more adequately met this need.

## APPENDIX TO CHAPTER 10

### Equilibrium Constants ( $K$ ) for Charge-Transfer Complexes of Maleic Anhydride with Various Comonomers<sup>a</sup>

Comonomer	$K$ (liter/mole)	Temperature (°C)	Solvent	Reference
Acetylene monomers				
Phenylacetylene	0.24	30	—	163
Acrylic monomers				
Acrylate, methyl	0.32	60	C <sub>6</sub> H <sub>12</sub>	29
Methacrylate, methyl	0.43	60	C <sub>6</sub> H <sub>12</sub>	29
Methacrylate, L-valine methyl ester	0.023	25	CH <sub>3</sub> CO <sub>2</sub> C <sub>2</sub> H <sub>5</sub>	398
Allyl monomers				
Allylbenzene	0.106	25	CHCl <sub>3</sub>	39
Allyl chloride	0.32	25	CHCl <sub>3</sub>	470
2-Allylphenol	0.06	25	CDCl <sub>3</sub>	46
Ester monomers, vinyl				
Acetate	0.060	25	CHCl <sub>3</sub>	152
	0.56	25	C <sub>6</sub> H <sub>12</sub>	153
	0.56	25	C <sub>6</sub> D <sub>12</sub>	152, 153
	0.25	60	C <sub>6</sub> H <sub>12</sub>	153
	0.066	25	CHCl <sub>3</sub>	151
Ether monomers, propenyl				
<i>cis</i> -Methyl	0.52	20	CHCl <sub>3</sub>	90
<i>trans</i> -Methyl	0.42	20	CDCl <sub>3</sub>	90
<i>p</i> -Propenylanisole	0.066	8.5	—	358
	0.059	21.9	—	358
	0.046	50.8	—	358
	0.043	60.0	—	358
Ether monomers, vinyl				
<i>n</i> -Butyl	0.56	20	CCl <sub>4</sub>	70, 114
	0.27	23	CHCl <sub>3</sub>	1068
	0.36	25	CHCl <sub>3</sub>	68
	0.30	37	CCl <sub>4</sub>	1068
	0.11	23	CH <sub>2</sub> ClCH <sub>2</sub> Cl	1068



Equilibrium Constants ( $K$ ) for Charge-Transfer Complexes of Maleic Anhydride with Various Comonomers<sup>a</sup>

Comonomer	$K$ (liter/mole)	Temperature (°C)	Solvent	Reference
Isobutyl	1.11	20	CCl <sub>4</sub>	70, 114
<i>tert</i> -Butyl	2.12	20	CCl <sub>4</sub>	65, 70, 114
2-Chloroethyl	0.13	10	CHCl <sub>3</sub>	75, 466
	0.10	30	CHCl <sub>3</sub>	75, 466
	0.09	51	CHCl <sub>3</sub>	75, 466
	0.29	30	C <sub>6</sub> H <sub>14</sub>	21, 114
	0.23	45	C <sub>6</sub> H <sub>14</sub>	21
	0.18	60	C <sub>6</sub> H <sub>14</sub>	21
Divinyl	0.036	25	CHCl <sub>3</sub>	114, 460
	0.036	25	CDCl <sub>3</sub>	126, 523
	0.036	24	CHCl <sub>3</sub>	474
	0.18	24	C <sub>7</sub> H <sub>16</sub>	65, 474
	0.108	24	C <sub>7</sub> H <sub>16</sub>	474
	0.098	38	CCl <sub>4</sub>	474
	0.08	25	CH <sub>3</sub> CN	521, 677
	0.0137	25	CH <sub>2</sub> Cl <sub>2</sub>	524
	0.013	24	CH <sub>2</sub> ClCH <sub>2</sub> Cl	474
	0.014	38	CH <sub>2</sub> Cl <sub>2</sub>	474
	0.014	24	CH <sub>2</sub> Cl <sub>2</sub>	474
1,2-Dihydroxy-benzene	0.243	—	—	1119
1,2-Bis-(hydroxy-ethoxy)benzene	0.280	—	—	1119
Ethyl	0.15	24	C <sub>7</sub> H <sub>16</sub>	65, 474
	0.041	25	CDCl <sub>3</sub>	126, 523
	0.017	15.5	CH <sub>2</sub> Cl <sub>2</sub>	412
Ether monomers, 1,1-disubstituted vinyl				
Diethoxy (Acrolein diacetal)	0.085	—	—	131
Ether monomers, 1,2-disubstituted vinyl				
Dimethoxy	0.16	12.5	CHCl <sub>3</sub>	466
(1,2-Dimethoxy-ethylene)	0.15	25	CHCl <sub>3</sub>	466
	0.13	50	CHCl <sub>3</sub>	466
	0.33	12.5	C <sub>6</sub> H <sub>6</sub>	466
	0.29	25	C <sub>6</sub> H <sub>6</sub>	91, 466
	0.22	50.5	C <sub>6</sub> H <sub>6</sub>	466
	0.16	25	C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub>	91, 466
	0.17	25	C <sub>6</sub> H <sub>5</sub> Cl	91, 466
	0.09	25	CH <sub>3</sub> COCH <sub>3</sub>	91, 466
Ether monomers, 2-phenylvinyl				
<i>n</i> -Butyl	0.20	30	CDCl <sub>3</sub>	88, 257
Isobutyl	0.30	30	CDCl <sub>3</sub>	88, 257
<i>sec</i> -Butyl	0.30	30	CDCl <sub>3</sub>	257
Ethyl	0.28	30	CDCl <sub>3</sub>	88, 257
Methyl	0.22	30	CDCl <sub>3</sub>	257
3-Methyl- <i>n</i> -pentyl	0.38	30	CDCl <sub>3</sub>	88, 275
<i>n</i> -Propyl	0.20	30	CDCl <sub>3</sub>	257
Isopropyl	0.20	30	CDCl <sub>3</sub>	257

Equilibrium Constants (*K*) for Charge-Transfer Complexes of Maleic Anhydride with Various Comonomers<sup>a</sup>

Comonomer	<i>K</i> (liter/mole)	Temperature (°C)	Solvent	Reference
Ether monomers, cyclic				
2,3-Dihydrofuran	0.045	25	CDCl <sub>3</sub>	115
2,5-Dihydrofuran	0.44	36	C <sub>6</sub> H <sub>14</sub>	21
	0.033	25	CHCl <sub>3</sub>	115
	0.30	47	C <sub>6</sub> H <sub>14</sub>	21
	0.18	60	C <sub>6</sub> H <sub>14</sub>	21
2,3-Dihydropyran	0.11	24	C <sub>7</sub> H <sub>16</sub>	65, 90, 474
	0.02	25	CH <sub>2</sub> Cl <sub>2</sub>	524
	0.035	25	CHCl <sub>3</sub>	90, 115
2,3-Dihydropyran, 2-Acetyl-2,5,6- trimethyl	0.03	25	CCl <sub>4</sub>	105
<i>p</i> -Dioxene	0.074	10	C <sub>6</sub> H <sub>6</sub>	466
	0.069	25	C <sub>6</sub> H <sub>6</sub>	94, 466
	0.058	51.5	C <sub>6</sub> H <sub>6</sub>	466
	0.047	25	CH <sub>3</sub> COCH <sub>3</sub>	94, 466
	0.040	25	C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub>	466
	0.055	10	CHCl <sub>3</sub>	466
	0.054	25	CHCl <sub>3</sub>	466
	0.040	51	CHCl <sub>3</sub>	466
	0.046	25	CHCl <sub>3</sub>	115
1,3-Dioxene, 2-isopro- penyl, 4-methyl	0.80	30	CCl <sub>4</sub>	133, 134
1,3-Dioxene, 2-Isopro- penyl 5,5-dimethyl	0.125	30	CCl <sub>4</sub>	133, 134
1,3-Dioxene, 2-styryl 4-methyl	1.27	30	CCl <sub>4</sub>	133, 134
1,3-Dioxane, 2-vinyl	1.01	37	C <sub>6</sub> H <sub>14</sub>	130, 132, 134
1,3-Dioxane, 2-furyl- 5,5-dimethyl	1.39	25	CCl <sub>4</sub>	114
1,3-Dioxane, 2-vinyl-5, 5-dimethyl	0.89	37	C <sub>6</sub> H <sub>14</sub>	130, 132
Furan	0.047	24	C <sub>7</sub> H <sub>16</sub>	106, 474
	0.03	20	CHCl <sub>3</sub>	416
	0.47	25	CDCl <sub>3</sub>	70
	0.09	24	CH <sub>3</sub> COCH <sub>3</sub>	109
	0.069	24	CHCl <sub>3</sub>	106
<i>p</i> -Oxathiene	0.030	11.5	C <sub>6</sub> H <sub>6</sub>	419
	0.029	20.0	C <sub>6</sub> H <sub>6</sub>	419
	0.028	30.0	C <sub>6</sub> H <sub>6</sub>	419
	0.027	40.0	C <sub>6</sub> H <sub>6</sub>	419
Olefin monomers				
Cyclohexene	0.01	36	C <sub>6</sub> H <sub>14</sub>	21
4-Cyanocyclohexene	0.51	25	—	527
Cyclopentene	0.03	22	CCl <sub>4</sub>	236
Vinylcyclohexane	5.81	12	CH <sub>3</sub> CO <sub>2</sub> C <sub>2</sub> H <sub>5</sub>	204
	2.34	26	CH <sub>3</sub> CO <sub>2</sub> C <sub>2</sub> H <sub>5</sub>	204

Equilibrium Constants (*K*) for Charge-Transfer Complexes of Maleic Anhydride with Various Comonomers<sup>a</sup>

Comonomer	<i>K</i> (liter/mole)	Temperature (°C)	Solvent	Reference
Vinylcyclohexane	2.21	20	CH <sub>3</sub> CO <sub>2</sub> C <sub>2</sub> H <sub>5</sub>	204
	1.88	25	CH <sub>3</sub> CO <sub>2</sub> C <sub>2</sub> H <sub>5</sub>	204
	1.67	30	CH <sub>3</sub> CO <sub>2</sub> C <sub>2</sub> H <sub>5</sub>	204
	1.59	35	CH <sub>3</sub> CO <sub>2</sub> C <sub>2</sub> H <sub>5</sub>	204
Vinylcyclohexane, <i>d</i> -methyl	10.40	12	CH <sub>3</sub> CO <sub>2</sub> C <sub>2</sub> H <sub>5</sub>	204
	2.54	16	CH <sub>3</sub> CO <sub>2</sub> C <sub>2</sub> H <sub>5</sub>	204
	2.44	20	CH <sub>3</sub> CO <sub>2</sub> C <sub>2</sub> H <sub>5</sub>	204
	1.90	25	CH <sub>3</sub> CO <sub>2</sub> C <sub>2</sub> H <sub>5</sub>	204
	1.79	30	CH <sub>3</sub> CO <sub>2</sub> C <sub>2</sub> H <sub>5</sub>	204
	1.70	35	CH <sub>3</sub> CO <sub>2</sub> C <sub>2</sub> H <sub>5</sub>	204
Olefin monomers, bicyclic				
Bicyclo[2.2.1]- heptene-2	0.015	22	CCl <sub>4</sub>	236
Isopropylidene dicyclo pentadiene, 5,6-dihy- droderivative	0.039	25	C <sub>6</sub> H <sub>14</sub>	240
Silane monomers				
Dimethyldivinyl	0.107	23	CDCl <sub>3</sub>	126
Triethoxy vinyl	0.36	18	CHCl <sub>3</sub>	405
Trimethyl vinyl	0.061	23	CDCl <sub>3</sub>	126
Styrene monomers				
Styrene	1.20	25	CHCl <sub>3</sub>	470
	0.33	30	C <sub>6</sub> H <sub>14</sub>	21, 236
	0.30	45	C <sub>6</sub> H <sub>14</sub>	20, 21
	0.26	60	C <sub>6</sub> H <sub>14</sub>	20, 21
	0.34	28	C <sub>6</sub> H <sub>14</sub>	1062
	0.24	20	CHCl <sub>3</sub>	151
	0.21	25	CH <sub>3</sub> COCH <sub>3</sub>	151
	0.25	60	C <sub>6</sub> H <sub>14</sub>	314
	0.21	38	CCl <sub>4</sub>	523
	0.27	25	CCl <sub>4</sub>	502
	0.29	—	—	527
	0.318	30	—	528
	0.289	60	—	528
	0.05	25	CHCl <sub>3</sub>	454
Styrene, <i>p</i> -dimethyl amino	0.50	25	C <sub>6</sub> H <sub>6</sub>	459
Sulfide monomers, vinyl				
Ethyl	0.035	15	CH <sub>2</sub> Cl <sub>2</sub>	264, 412
	0.09	25	CH <sub>2</sub> Cl <sub>2</sub>	264, 265
Isobutyl	0.035	25	CH <sub>2</sub> Cl <sub>2</sub>	264, 265
Phenyl	0.090	15	CH <sub>2</sub> Cl <sub>2</sub>	264, 412
Sulfide monomers, 2-phenylvinyl				
Isobutyl	0.40	30	CDCl <sub>3</sub>	81, 89
Ethyl	0.25	30	CDCl <sub>3</sub>	88, 89
<i>n</i> -Propyl	0.38	30	CDCl <sub>3</sub>	88, 89



Equilibrium Constants (*K*) for Charge-Transfer Complexes of Maleic Anhydride with Various Comonomers<sup>a</sup>

Comonomer	<i>K</i> (liter/mole)	Temperature (°C)	Solvent	Reference
Isopropyl	0.28	30	CDCl <sub>3</sub>	88, 89
Sulfide monomers, cyclic				
Oxathiene (see cyclic ethers)				
Thiophene	0.02	—	—	416
<i>N</i> -Vinyl heterocyclic monomers				
Caprolactam	0.20	20	CHCl <sub>3</sub>	179
Phthalimide	0.76	25	CDCl <sub>3</sub>	171, 182
	0.05	25	DMF	171, 182
Succinimide	0.84	25	CDCl <sub>3</sub>	171, 182
	0.09	25	DMF	171, 182
Pyrrolidone	1.20	25	CDCl <sub>3</sub>	171, 182
	0.44	25	DMF	171, 182
	0.097	25	CH <sub>3</sub> COCH <sub>3</sub>	170
	0.060	25	CH <sub>3</sub> CO <sub>2</sub> C <sub>2</sub> H <sub>5</sub>	170
	0.178	25	CHCl <sub>3</sub>	170
	0.119	25	ClCH <sub>2</sub> CH <sub>2</sub> Cl	170
	0.336	25	C <sub>6</sub> H <sub>6</sub>	170
Miscellaneous aromatic monomers				
Benzofuran	0.01	25	C <sub>6</sub> H <sub>12</sub>	116
Benzothiophene	0.34	27	CHCl <sub>3</sub>	116
Indole	0.28	20	CHCl <sub>3</sub>	116
Indole, 1-vinyl	0.25	25	CDCl <sub>3</sub>	183
Indene	0.32	25	CH <sub>3</sub> CO <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	371
	0.16	45	CH <sub>3</sub> CO <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	371
2-Isopropenyl-napthalene	0.17	20	CH <sub>2</sub> Cl <sub>2</sub>	788
	0.23	25	CH <sub>2</sub> Cl <sub>2</sub>	1066
Phenanthrene	0.16	25	CHCl <sub>3</sub>	369
Stilbene, <i>trans</i> -	0.150	25	CHCl <sub>3</sub>	355
	2.020	25	C <sub>4</sub> H <sub>8</sub> O	355
	0.210	35	CH <sub>3</sub> CO <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	1134

<sup>a</sup> Equilibrium constants determined by procedures described in References 457–461. No attempt has been made to evaluate reported values.

# GRAFT COPOLYMERS

## 11.1. INTRODUCTION

Considerable effort has been spent on developing methods for grafting MA or MA copolymers to the backbone of a variety of saturated and unsaturated polymeric materials. In general, MA grafting has been and is continuing to be explored as a technique to improve the physicochemical properties of various polymers, by providing polarity to promote hydrophilicity, adhesion, and dyeability, give functionality for crosslinking and other chemical modifications, promote compatibility with other polymers and fillers, and provide improved heat resistance. In rubber chemistry, grafting has been investigated for producing materials with improved green strength, vulcanization and fatigue properties, as well as decreasing the oxidizability of the materials. The techniques explored have included free radical, “ene” (see Chapter 5), and Diels–Alder (see Chapter 4) type reactions. In graft copolymers the backbone and side chains may both be homopolymeric; the backbone may be homopolymeric and the side chains copolymeric; or vice versa; or both the backbone and side chains may be copolymeric but of different chemical composition. To varying extent, all these conditions have been explored for MA, with much of the effort disclosed in the patent literature. These grafting studies are reviewed and discussed, along with providing a comprehensive patent listing on MA graft copolymers showing the many possible uses that exist for such materials.

### 11.1.1. Polyethylene

Maleic anhydride may be grafted to polyolefins, such as polyethylene, by mechanochemical,<sup>(1–5)</sup> mechanochemical with free-radical initiators,<sup>(177)</sup> free radical,<sup>(6,7,133)</sup> ionic,<sup>(8)</sup> and radiation-initiation<sup>(10)</sup> techniques. The solid-phase mechanochemical modification studies were run by a low-temperature mechanical dispersion,<sup>(1,133)</sup> extruder,<sup>(2,5)</sup> die extruder,<sup>(3)</sup> and grinding<sup>(4)</sup> techniques. Modification of polyethylene with  $\leq 20\%$  MA leads to crosslinking during extrusion of the polymer–anhydride blend in the extruders.<sup>(2)</sup> This crosslinked material generally retains its form during heating to  $>300^\circ\text{C}$ .

Kneading a mixture of the polyethylene, free-radical initiator and MA below the decomposition temperature ( $T$ ) of the radical initiator, subjecting it to shear forces, and heating to a temperature above  $T$  is reported to give uniform grafting with substantial reduction of crosslinking.<sup>(177)</sup> Extrusion of



the grafted material at 150°C helped reduce the crosslinking. Grafting of MA to polyethylene may be accomplished by degrading the polyolefin in an extruder at 420°C and heating with 10% MA in a Dowtherm-heated autoclave for 90 min at 220°C.<sup>(9)</sup> Nongrafted MA is recovered by evaporation at 5 mm Hg, giving a product with about 3% grafted anhydride. Products of this type are waxy materials, exhibiting improved adhesion to polar textiles, metals, and plastic films.

Kinetics of alkenylation of MA by polyethylene has been studied over the 190–275°C range.<sup>(166)</sup> The product yield increased with time and then remained constant at  $\leq 200^\circ\text{C}$ ; at higher temperatures the yield reached a maximum and then decreased as longer reaction times led to tar formation. Low-density polyethylene films, having a molecular weight of 17,000, have also been grafted with MA by starting with poly(maleic anhydride). The reactions were run in acetic anhydride at 80–110°C, using benzoyl peroxide (BPO) and azobisisobutyronitrile (AIBN) initiators.<sup>(6)</sup> Grafting in air with AIBN appears to go best. The results showed that polyethylene macroradicals are formed through the decomposition of hydroperoxide and peroxide groups. Side chains of poly(maleic anhydride) are formed by the combination of polyethylene macroradicals with those of poly(maleic anhydride). The mechanism was confirmed by the influence of the amount of film, the initiator and anhydride concentrations, and temperature versus the percentage of grafting.

The effect of polymer concentration on the grafting of MA on polyethylene has also been studied in xylene solvent at 90–130°C, using BPO initiator.<sup>(7)</sup> The character of the reaction curves obtained at different polymer, monomer, and initiator concentration and the various temperatures showed the importance of the termination reactions and the appearance of the “gel effect” at higher polymer concentrations.<sup>(148)</sup> The gel effect was influenced not only by the primary viscosity but also by viscosity changes during the reactions. Since alkylbenzene–MA reactions are known (see Chapter 6) and since it is known that solvents may form charge-transfer complexes with MA (see Chapters 6 and 10), it would be interesting to repeat this work in a variety of solvents, looking at both grafting and side reactions.

Grafting of MA on polyethylene in a heterogeneous mixture, in the presence of dichlorobenzoyl peroxide and small amounts of other vinyl monomers, appears to be an attractive grafting technique.<sup>(178)</sup> The fairly high grafted materials may be readily isolated as powders or pellets from the alkyl acetate–alcohol reaction medium.

Grafting of MA with ionic initiators on low-density polyethylene films has also been briefly studied and shown to be best achieved in acetic anhydride solvent,<sup>(8)</sup> using  $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$  catalyst at 110°C. A red-colored powder, with variable composition, derived from the  $\text{SnCl}_5 \cdot 5\text{H}_2\text{O}$  reaction with acetic anhydride was reported to be the initiator for the grafting reaction.

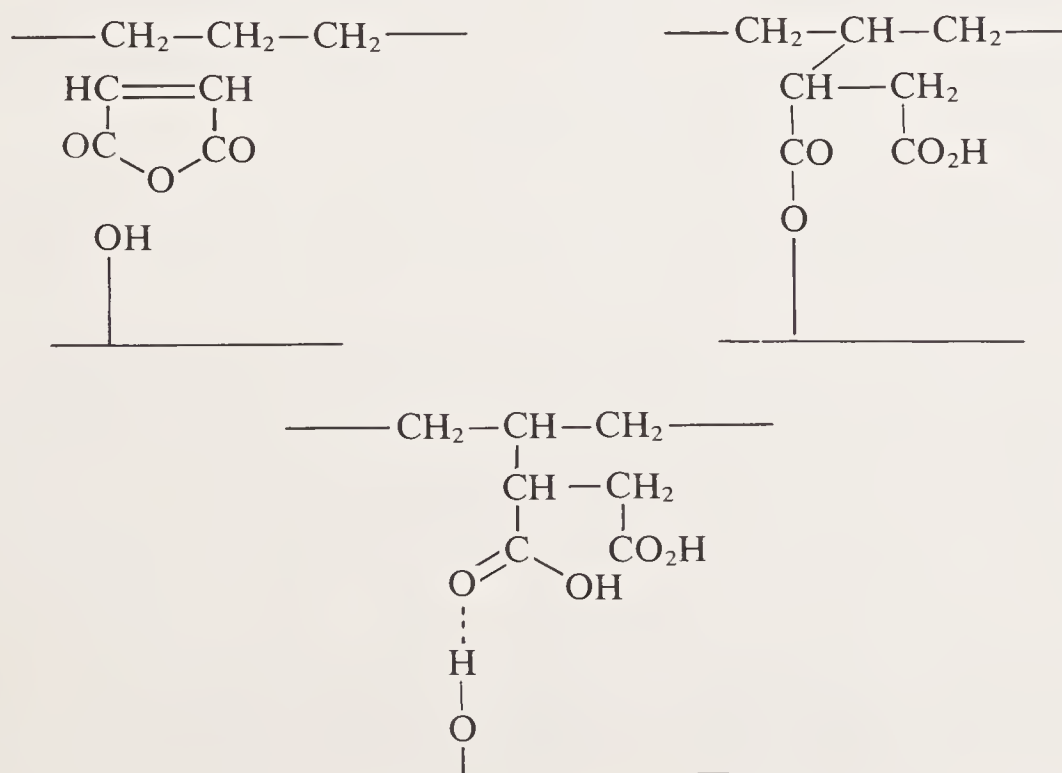


Solvent extraction and infrared spectra studies clearly showed grafting was achieved.

The reaction between irradiated polyethylene film and molten MA occurs at temperatures  $\geq 120^\circ\text{C}$  to form grafted polymer, which is insoluble in boiling aromatic solvents.<sup>(10)</sup> The grafted polymer, which is more friable than ungrafted polyethylene, decomposes on heating without melting. The grafted materials also fail to exhibit the elasticity of typical polyethylene. Attempted direct grafting by irradiation ( $^{60}\text{Co}$ ) of benzene and acetone solutions of polymer and anhydride failed.

The wettability and adhesive properties of MA-grafted polyethylene have been well studied.<sup>(11,12)</sup> The low level grafted materials studied, with  $(16.0\text{--}20.0) \times 10^5$  groups/ $\text{cm}^2$ , were prepared by free-radical polymerization of MA on the surface of low-density polyethylene. After hydrolysis, the grafted materials were equilibrated with solutions of different alkali and organic cations at constant pH. The wettability of the grafter polymers, as studied by contact angle measurements, varied with both the nature of the cations studied, and the pH of the wetting solution.<sup>(12)</sup> At pH 7.5, it was shown that wettability varied in the order  $\text{Ca}^{2+} > (\text{CH}_3)_4\text{N}^+ > \text{K}^+ > \text{Na}^+ > \text{NH}_4^+ > \text{Li}^+$ . Blends of MA-grafted polyethylene with atactic polypropylene have been shown to be good shoe sole adhesives.<sup>(11)</sup> The improved adhesion of the polyolefins to the shoe sole substrates was attributed to dispersion, hydrogen bonding, and other forces introduced by the grafted MA and maleic acid residues.

Gaylord and coworkers<sup>(13,168)</sup> recently presented evidence to show that the compatibilization of the low- and high-density polyethylene and kaolin or bentonite clays in the presence of MA involves both grafting and anhydride-hydroxyl reactions. The peroxide-catalyzed reactions were studied in a Brabender Plasticorder at  $130\text{--}165^\circ\text{C}$ .<sup>(13)</sup> Presumably the *in situ* grafting and condensation reactions occurred as follows:



With up to 40% clay, the compatibilized polymer/clay composites exhibit lower water vapor permeability than typical unfilled polyethylene. The compatibilized composites containing the clay particles were crosslinked, with the anhydride-grafted polyethylene bonded to the clay particles and uncrosslinked polyethylene. The composites exhibited improved flexural modulus, break strength, and notched Izod impact properties.<sup>(13)</sup>

Chlorocarboxylation of high-density polyethylene, i.e., simultaneous introduction of both carboxyl and chlorosulfonyl groups on the polymer surface, has been accomplished with MA-sulfonyl chloride mixtures.<sup>(14)</sup> The same type grafting reaction occurs with chloromaleic anhydride and maleimides. The carboxylic elastomeric materials contained 32.5–57.1% Cl and 0.59–4.05% carboxyl groups. The polymers resembled chlorosulfonated polyethylene in physicomachanical properties. Polypropylene is resistant to the same reaction. A typical graft copolymer, having 56.4% Cl and 2.38% carboxyl, was blended with MgO, ZnO, and stearic acid and vulcanized in a mold at 150°C for 10 min to give an elastomer showing 600% elongation and tensile strength of 120 kg/cm<sup>2</sup>. It is interesting to note that maleimides are also useful as crosslinkers for chlorosulfonated polyethylenes,<sup>(157)</sup> through the sulfonyl chloride cure sites. The reaction mechanism has not been totally clarified. Carbon black reinforced vulcanizates prepared by this technique exhibit outstanding compression set resistance, good resistance to heat aging, and excellent stress-strain properties.

Derivatives of MA, such as fumarates, maleates, and maleimides have also been grafted to polyethylene, as a technique to change surface properties and crosslink the polymer.<sup>(154,155,182)</sup> Using dicumyl peroxide, 1,1,2,2-tetrahydroperfluoroalkyl fumarates were grafted to high-pressure polyethylene at 160°C. The product with a critical surface energy of 15.6 dynes/cm, compared to 31.0 dynes/cm for ungrafted material, is useful in biomedical applications because of reduced tendency to coagulate blood. Maleimide-grafted polyethylenes, prepared by irradiating blends of polyolefin with maleimides, are useful for preparing improved packaging laminates.<sup>(182)</sup>

### 11.1.2. Polypropylene

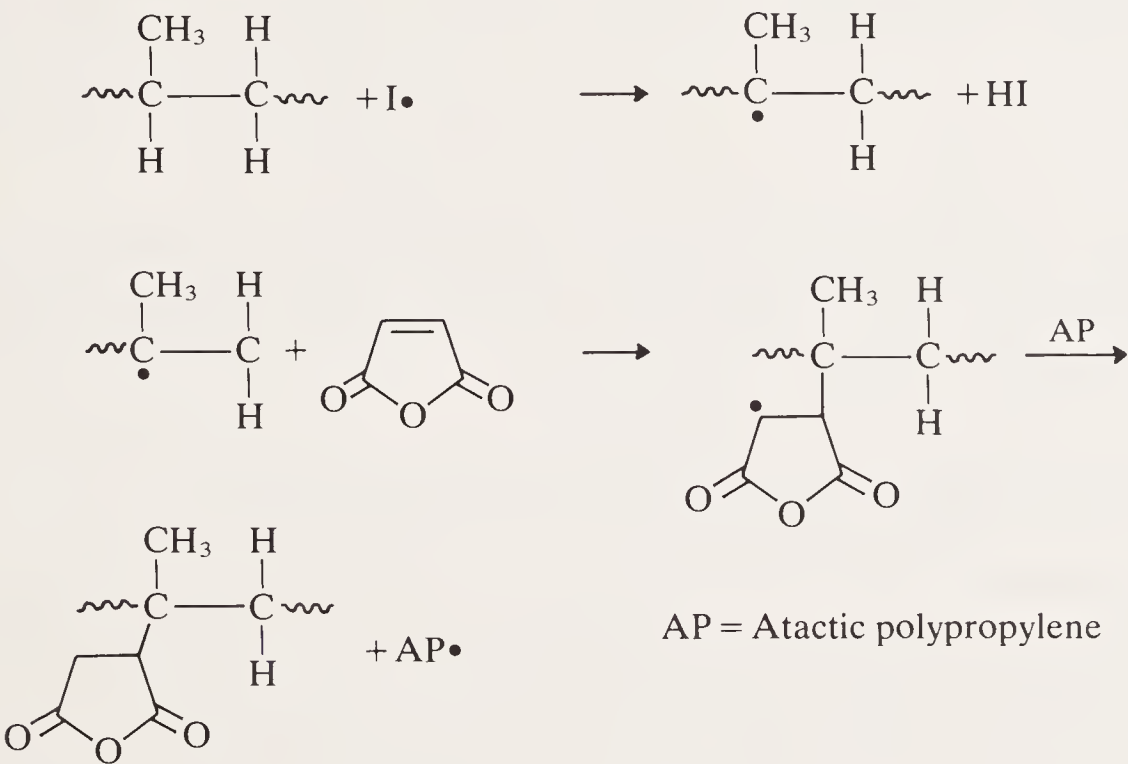
Grafting of MA on both isotactic and atactic polypropylene has been studied under a variety of conditions.<sup>(15–25,52,179)</sup> Maleic anhydride, maleic acid, and monomethyl maleate have also been grafted to polypropylene by a thermal process at 325°C.<sup>(52)</sup> Mechanochemical modification of both atactic<sup>(23)</sup> and isotactic<sup>(20)</sup> polypropylene may be accomplished by blending polymer-anhydride mixtures in laboratory mills with peroxide initiators. Mechanochemical grafting can also be brought about by using peroxidized polypropylene.<sup>(20)</sup> Extraction studies clearly showed grafting was achieved.<sup>(16,23)</sup> An additional reaction of MA with isotactic or atactic polypro-



pylene was observed in the presence of radical initiators and sunlight, using benzene or xylene solvents.<sup>(18,20,22)</sup> The homogeneous grafting of MA to polypropylene was studied in xylene over the 80–120°C temperature range with BPO initiator.<sup>(22)</sup> The products were precipitated by methyl alcohol, washed, and dried. The infrared spectrum showed bands for anhydride (1 840 and 1 775 cm<sup>-1</sup>) and methyl ester carbonyl (1 710 and 1 200–1 300 cm<sup>-1</sup>) formed during workup. The incorporation of MA produces large increases in the tensile strength, elongation, and hardness of atactic polypropylene (Table 11.1). Little deterioration of the polymer was detected. The reaction rate expression ( $R_p$ ) for the solution grafting was as follows:

$$R_p = k[\text{Atactic polypropylene}] [\text{MA}] [\text{Initiator}]^{1/2}$$

The order of efficiency of various free-radical initiators followed the order dicumyl peroxide > di-*tert*-butyl peroxide > BPO > AIBN.<sup>(22)</sup> The mechanism proposed for the grafting reaction is envisioned as follows:



Maleic anhydride has been grafted to polypropylene by heating with BPO or *t*-butyl peroxybenzoate in refluxing chlorobenzene.<sup>(21,180)</sup> The level of anhydride grafting on the isolated products, recovered by precipitation with

Table 11.1. Properties of MA–Polypropylene Grafts<sup>a</sup>

Material	Tensile strength (kg/cm <sup>2</sup> )	Elongation (%)	Hardness
Atactic polypropylene	5.4	110	10–15
Graft (4.5% MA) <sup>b</sup>	19.5	400	50–55

<sup>a</sup> After Reference 22. By permission of John Wiley & Sons, Inc., New York, New York.  
<sup>b</sup> Grafted polymer soluble in benzene, toluene, xylene, and carbon tetrachloride.



acetone, varied from 0.4 to 3.3% in accordance with the amount of MA charged. The grafting of MA on polypropylene has also been achieved in heptane at 200°C, with di-*t*-butyl peroxide initiator, and at 325°C by a thermal process.<sup>(52)</sup> Materials of this nature, with low levels of grafting, are low-viscosity waxes useful as adhesives for aluminum–paper laminates.

The surface of highly oriented polypropylene fibers have been modified by vapor-phase grafting of MA.<sup>(19)</sup> Little is known about the properties of these grafted fibers. However, the graft sites on the fibers are useful for joining the fibers directly into nonwoven fabrics.

Maleic anhydride grafted polypropylene may be easily vulcanized with diamines and magnesium oxide. Crosslinking with compounds such as Zn, Pb, or Mg(OAC)<sub>2</sub> gives insoluble, elastic, ionic salts. The ionic crosslinking produces materials with high softening temperatures and thermal stability.<sup>(17,20–22)</sup> The melting point jumped from 55°C for the graft (4.5% MA) to 195–200°C for the alkali salts, 165°C for the lead salt, and 230°C for the magnesium salt.<sup>(22)</sup> The grafted materials aid in the dispersibility of polypropylene with Nylon 6.<sup>(26,27,149)</sup> Presumably the increased dispersibility is attributed to the reaction of the MA moiety on the polypropylene with the Nylon amino residues. The existence of such bonding was supported by the infrared spectra and differential scanning calorimetry studies.<sup>(26)</sup>

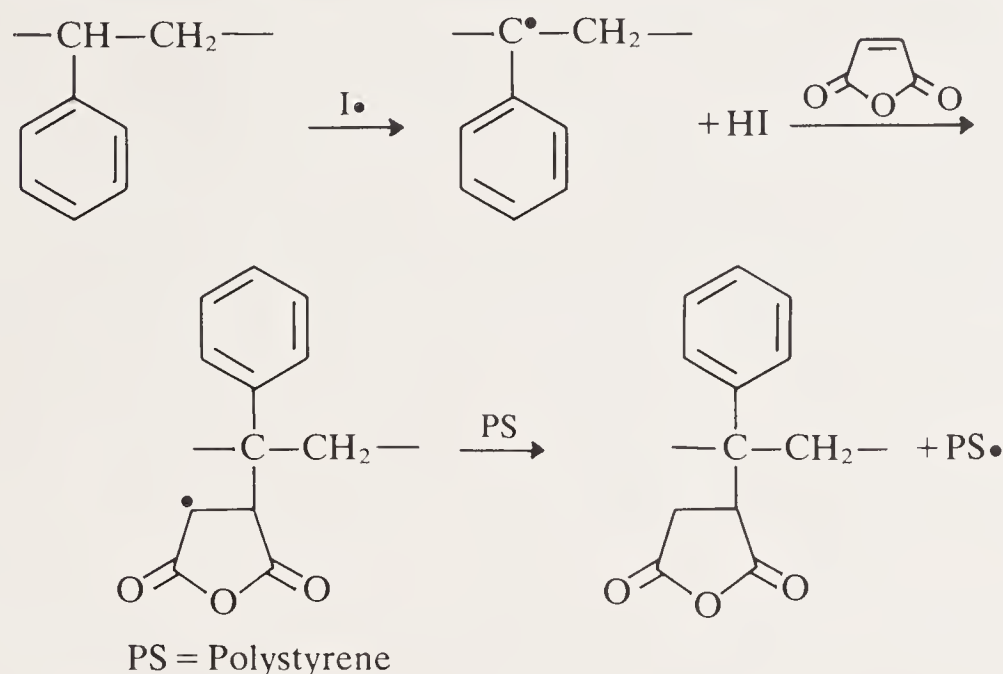
Isotactic polypropylene–glass fiber blends with dibenzothiazolyl disulfide and bis(maleimides) have been extruded to obtain moldings with improved impact and flexural strength.<sup>(183)</sup>

### 11.1.3. Other Saturated Polymers and Copolymers

Mechanochemical and thermal processes have been used to graft MA to poly(isobutylene)<sup>(26,169)</sup> and poly(vinyl chloride).<sup>(28)</sup> Mechanochemical grafting of MA–methyl methacrylate copolymers on PVC has also been explored, with the desire to improve heat resistance and processability.<sup>(28)</sup> The grafting was shown to occur as a result of polymeric macroradical formation. Triethanolamine promoted the PVC grafting reactions.<sup>(28)</sup> Contrary to expectations, the MA-grafted PVC materials exhibited reduced thermal stability. Other than heat stability, very little is published about the properties of the resultant grafted PVC copolymers.

Grafting of MA on PVC with peroxide initiators has also been explored.<sup>(111)</sup> The reactions were run in the molten state with dicumyl peroxide. The degree of maleation increased with increasing degree of polymerization of PVC and with increasing peroxide and MA contents. Optimum conditions were 140°C for 10 min. Treating the maleated PVC with metal oxides produced new ionomer films, with tensile strength, hardness, and softening temperatures greater than the parent PVC films. Treatment of the hydrolyzed grafted polymers with polyisocyanates provides a method to prepare potentially useful crosslinked PVC foams.<sup>(112)</sup>

Maleic anhydride may be grafted to polystyrene by both free-radical,<sup>(27,29)</sup> photochemical,<sup>(29-31,77,84)</sup> and cationic<sup>(176)</sup> initiation techniques. Photochemical grafting of MA on styrene-methyl methacrylate copolymers have also had some study.<sup>(84)</sup> Using di-*tert*-butyl peroxide, polystyrene-MA graft copolymers have been prepared that contain 2–15% pseudosuccinic anhydride residues. The mechanism for the reaction is envisioned as follows:



Photochemical addition of MA to polystyrene has been observed in dioxane solvent, using photosensitizers and radiation with  $\lambda > 340$  nm.<sup>(27,30,31)</sup> It is thought that the sensitized photoaddition proceeds via an attack by the excited anhydride triplet state on the charge-transfer complex between the anhydride and the aromatic nucleus. Photochemical reaction of benzene and alkyl substituted aromatics with MA are known to give a variety of potentially useful products (see Chapter 6).

The MA-grafted polystyrene materials are claimed to be useful as vulcanizing agents for rubber<sup>(27)</sup> and a modifier for improving the structure properties of calcium silicate filled high-pressure polybutylene composites.<sup>(32)</sup>

The phenyl groups on polystyrene have also been modified by treatment with MA using cationic catalysts such as boron trifluoride to obtain carboxylated materials.<sup>(176)</sup> Properties of these materials remain to be studied.

Until they are vulcanized, elastic, amorphous ethylene-olefinic copolymers have very little possible utility except as components of caulks or sealants. However, grafting MA on the copolymers, using peroxide initiators, and compounding the modified materials with zinc oxide provides improved rubbers.<sup>(33)</sup> A typical recipe would consist of 100 parts ethylene-propylene copolymer, 20 parts zinc oxide, 7 parts MA, and 2 parts BPO. Curing is carried out at 160°C for 30–45 min. Previously grafted copolymers, containing 2–5 MA residues, can also be cured with *N*-phenyl-*B*-naphthylamine initiator, steric acid modifier, and zinc oxide crosslinker.

Grafting of MA on ethylene-propylene copolymers has also been studied in bulk at 200°C<sup>(162)</sup> and in refluxing chlorobenzene in the presence of



di-*t*-butyl peroxide.<sup>(163)</sup> Chlorinated ethylene–propylene materials (1.5% Cl) were grafted with MA in *o*-dichlorobenzene at 180°C. Post treating the chlorinated grafts with amines produced detergent additives for lubricants.<sup>(164)</sup> The patent literature<sup>(177)</sup> discloses that maleimides have also been grafted on ethylene–propylene copolymer for production of polyester polyblends with improved impact strength.

Using BPO and AIBN, solutions of ethylene–vinyl acetate copolymers have been grafted with MA.<sup>(34–37)</sup> Grafting is assumed to occur via ethylene–vinyl acetate macroradicals formed by chain-transfer reaction of the copolymer with initiator radical moieties. Differential thermal analysis indicated that the graft copolymers had a crystalline melting point of ca. 100°C.<sup>(35)</sup> The reaction has been modified to include grafting of MA-co-(meth)acrylates on the ethylene–vinyl acetate copolymers.<sup>(159)</sup> The graft copolymers have excellent adhesive properties and can be used as the main component of melt adhesives for metals and plastics. It is also known that fumaric acid may be grafted to ethylene–co–vinyl acetate polymers, with peroxide initiators, to obtain useful laminating and molding resins.<sup>(38)</sup>

Recent patents disclose that *N*-alkyl and *N*-aryl substituted maleimides have been grafted to poly(vinyl acetals),<sup>(156,184)</sup> and polystyrene or styrene copolymers.<sup>(185,186)</sup> The grafted poly(vinyl acetals), with molecular weights of the order of 80,000–250,000, are suitable binders for film materials, adhesives, and coatings. The maleimide grafted polystyrenes may be fabricated into moldings with improved impact, flexural strength, and heat distortion temperature.

#### 11.1.4. Polyisoprene

Reactions of MA with both natural and synthetic rubber has had substantial study.<sup>(36–51,53–70)</sup> Maleinated rubbers may be prepared by three techniques: thermal initiation,<sup>(51,54,57,63,65)</sup> peroxide initiation,<sup>(42,56,57,63,65)</sup> and initiation by mastication.<sup>(41,49,50,53,55,67,70)</sup> Free-radical and radiation-initiated reactions of rubber with MA and with several maleimides have also been described.<sup>(160,167)</sup> Since treatment of rubber with MA readily generates substantial amounts of insoluble polymer, the reaction is more appropriately called a crosslinking reaction.<sup>(60,61)</sup> The reaction is discussed in this graft section because of similarity to conventional grafting and ease of discussion in this section.

Thermal initiation for the rubber maleination reaction requires a temperature >160°C and preferably about 220–240°C, along with a considerable excess of MA. Maleates and maleimides also undergo thermal addition to rubber under the same conditions. The maleination reaction is promoted by the addition of a variety of initiators, such as BPO, AIBN, dibenzothiazil disulfide, and ascaridol;<sup>(56)</sup> however, oxygen inhibits the reaction.<sup>(65)</sup> The



products obtained by thermal and free-radical initiation are not the same, as shown by infrared spectra.<sup>(57)</sup> The spectra show that the thermal process introduces additional unsaturation into the polymer molecule. Using peroxides, the reaction proceeds well in dilute solution at temperatures in the range 70–80°C; however, about 10 wt. % BPO, based on rubber, is required. Azobisisobutyronitrile works better to reduce the gelation tendency of the rubber, but even so it is still not practical to exceed 2% rubber concentration.<sup>(58)</sup> Products ranging from elastomeric to hard resinous materials have been made and studied, containing up to 50% combined MA (1 mole per C<sub>5</sub> unit).<sup>(44,46)</sup>

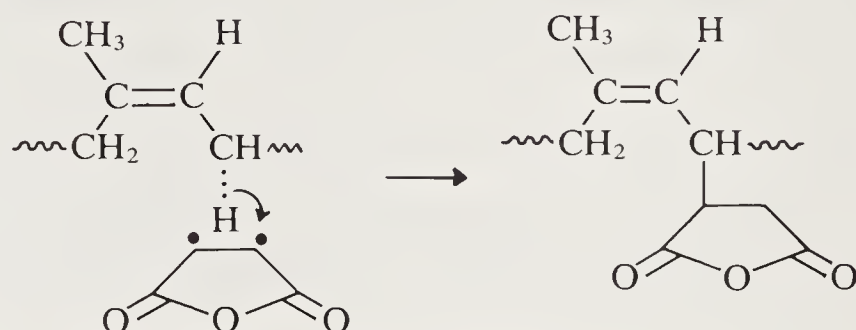
Up to 6% MA can be easily combined with rubber in a mixing machine. Initially the mixture is lacy and crumbly, but continued milling consolidates the mass and gives a product that can be processed like ordinary rubber.<sup>(47,70)</sup> During the milling process both crosslinking and maleination occur simultaneously,<sup>(53)</sup> to give materials with a lower degree of thermoplasticity.<sup>(40)</sup> Addition of monomer such as methyl methacrylate and styrene during mechanochemical modification helps retard and/or regulate gel formation.<sup>(67,68)</sup> The additional vinyl monomer improves grafting of MA to the rubber.<sup>(68)</sup> Styrene addition may be used to prepare rubber with pendent styrene-co-MA grafts.<sup>(68)</sup> The reactions of rubber with MA under mechanical stress were shown to be independent of the oxygen content in the atmosphere from 20 to below 5% oxygen.<sup>(49,50)</sup>

It has been shown that natural rubber and MA reactions are best run in the presence of compounds such as 2,6-di-*tert*-butyl-*p*-cresol, 6-phenyl-2,2,4-trimethyl-1,2-dihydroquinoline, and  $\beta$ -dicarbonyl compounds as antioxidants.<sup>(41,46,51,181)</sup> Both for the mass and solution production procedures at 180°C, these reagents inhibit crosslinking. Recent patents<sup>(162)</sup> claim that triazine derivatives, such as 2,4,6-trichloro-5-triazine,<sup>(152)</sup> and phosphorus compounds, such as trioctadecylphosphite,<sup>(152)</sup> are also very effective for preventing crosslinking during treatment of liquid rubbers with MA.

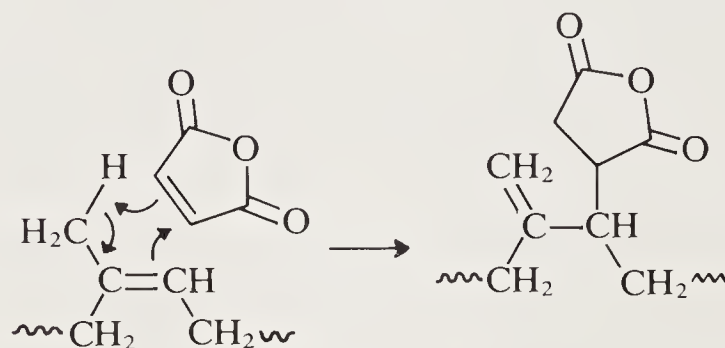
Natural rubber, due to the double bonds and 2-methylenic carbons, is highly sensitive to oxygen. It has been shown that the oxidizability of rubber is significantly reduced when the rubber is treated with MA.<sup>(48,59,66)</sup> For example, crude rubber containing 9% MA is ten times as resistant to oxidation after 200 h at 80°C as purified crude rubber and comparable to isobutylene-isoprene elastomer.<sup>(6)</sup> It is claimed that the MA reaction blocks the 2-methylenic carbons to bring about the reduced oxidizability.<sup>(35,59)</sup> However, the maleinated materials have improved resistance to oxygen far greater than expected for the percent modification.<sup>(48,59)</sup> The grafted materials also exhibit improved green strength,<sup>(67)</sup> reduced scorching tendency during vulcanization,<sup>(62)</sup> and improved fatigue life,<sup>(57)</sup> without loss of elasticity.<sup>(56)</sup>

A great amount of analytical data has been collected on the reaction of natural rubber with MA.<sup>(52,59,72,73,194,195)</sup> Two structures have been proposed

for maleinated rubber prepared thermally. Farmer<sup>(72)</sup> suggested that MA was combined in accordance with the “substitutive addition” scheme proposed by Alder and coworkers<sup>(74,75)</sup>:



This is a free-radical-type reaction scheme, first adopted for maleinated rubbers or materials prepared chemically and/or in the presence of free-radical initiators. For the reaction, it is assumed that heat, in the same way as an initiator, allows the labile hydrogen atom to be removed. Pinazzi *et al.*<sup>(56)</sup> proposed a more plausible reaction scheme, based on purely thermal reactions that take place in a neutral medium without formation of any ion or free radical.



The second mechanism corresponds to a heat-initiated, concerted electronic-transfer-type “ene” reaction (see Chapter 5), which explains how thermal and radical grafting produces different products.<sup>(57)</sup> In the absence of initiators, the second reaction is believed most probable.<sup>(59)</sup> The lack of effect of mercaptans (benzenthionol) on the reaction supports the mechanism, along with the clear evidence for double-bond movement during reaction. However, additional evidence shows that crosslinking and polymeric side-chain formation complicates the picture.<sup>(60,61)</sup> In the ene grafting mechanism, each combined anhydride blocks a methylenic carbon in the position of the polymer double bond, precisely the one susceptible to oxidation. Thus, this mechanism more adequately explains how thermal grafting of MA can improve the oxidizability of rubber.

High-resolution nuclear magnetic resonance studies of MA modified *cis*-1,4-polyisoprene shows that MA is preferentially linked by inter or intramolecular additions to the double bond of the isoprene unit.<sup>(173)</sup> The reaction is accompanied by ring formation and oxidation of the rubber.

Maleinated rubbers have been successfully treated with metal oxides, diols, amines, and isocyanates, to give rubber products with improved flex



life and tear resistance.<sup>(79,174)</sup> Modification of isoprene containing elastomers with maleimides and bismaleimides also provides a very effective means of accelerating curing or vulcanization of the materials with ionizing radiation.<sup>(160)</sup> Furthermore, the use of bismaleimides as modifiers for vulcanization of rubbers promotes adhesion of the materials to polyolefins<sup>(175)</sup> and other tire cord materials.<sup>(187,188)</sup> The reaction of bismaleimides with isoprene copolymers has also been explored and patented as a technique for producing photocurable elastomers.<sup>(191)</sup> Blends of polycarbonates with maleimide-grafted elastomers provides molding materials with improved processability and high-dimensional stability.<sup>(192)</sup>

High performance rubbers may be prepared from MA-modified polyisoprene.<sup>(158)</sup> Polyisoprene, having a molecular weight of 42,000 and containing 81% *cis*-1,4-bonding, is grafted with MA in toluene solution at 150°C for 7 h. The grafted polymer solution is combined with methyl alcohol to isolate the modified material, containing 4.1 mol % MA. Blends of the polyisoprene with carbon black, stearic acid, zinc stearate, zinc oxide, and an antioxidant were molded in a hot press. The product showed breaking strength of 71.2 kg/cm<sup>3</sup>, elongation of 400%, and hardness of 74.

Maleic anhydride may be grafted to scrap vulcanized rubber to aid in reclaiming of natural rubber and GR-5 scraps.<sup>(77,78)</sup> These materials have a higher Mooney viscosity, with less tendency to sag or flow on storage. Revulcanization can be achieved with different cure systems to give vulcanizates with improved oil resistance.

#### 11.1.5. Butadiene Polymers and Copolymers

Polybutadienes<sup>(45,80–84,165)</sup> and polychloroprene,<sup>(85)</sup> as well as styrene-butadiene,<sup>(84,86,87)</sup> butadiene-acrylonitrile,<sup>(71)</sup> and dehydrated poly(vinyl alcohol)<sup>(89)</sup> copolymers, have been treated with MA to obtain graft copolymers. Liquid polybutadienes, containing both 1,2- and 1,4- polymerization residues, react vigorously with MA at 270°F to yield a solid gel, insoluble in water, caustic, and organic solvents.<sup>(80)</sup> The reaction is catalyzed by peroxides and may involve copolymerization, crosslinking, and Diels–Alder addition of anhydride. The reaction is moderated by solvents such as xylene but still produces highly crosslinked materials. Heating liquid butadiene oligomers (mol. wt. 1 500) with MA in 1:0.05–0.35 mole ratio (calculated on monomer units) at 220–230°C is claimed to give solid or liquid copolymers in high yield.<sup>(83)</sup> Hydrolysis of these materials with aqueous solutions of alkylamines at ≤30°C gives modified rubbers useful in leather treatment and adhesive applications.<sup>(82)</sup>

Grafting anionically prepared polybutadiene with MA, in a 4:1 weight ratio, at 200°C gave copolymer with 16% grafted anhydride.<sup>(165)</sup> Ammonolysis gave a water-soluble amide–ammonium salt useful in waterborne coatings.



The product was also useful for producing hard, flexible, adherent wire coatings.

Modification of low-molecular-weight poly(butadiene) with MA does not change the fundamental mechanism of crosslinking, which occurs by radical polymerization of double bonds, only its kinetic parameters and crosslinking density.<sup>(45)</sup> The crosslinking reaction order, activation energy, and heats of reaction were recently studied, using differential scanning calorimetry techniques.<sup>(45)</sup> The grafted materials studied contained 0.55–4.95 mole MA per 100 C<sub>4</sub> units and the molecular weight between crosslinks for the materials was 117–216. Thermogravimetric analysis shows the thermal stability of the grafted polymer to be lower than that of the unmodified material. Weight loss studies show the grafted polymer suffers a step-by-step thermal destruction reaction, with the first step being zero order and the second step being a first-order reaction. The activation energies for the two reactions were 18.4–27.1 and 68.9–87.6 kcal/mol, respectively.

Gancarz and Laskawski<sup>(45,170)</sup> also prepared and studied low-molecular-weight polybutadienes grafted with MA-co-styrene alternating copolymer. As expected, styrene greatly facilitated MA grafting, confirming earlier work by Gaylord.<sup>(133)</sup> Also, the curing rate of the copolymer prepared from this type of grafting was enhanced, when compared with the cure rate of the ungrafted and MA-grafted polybutadienes. However, the highest rate of thermal decomposition was observed from the MA-co-styrene grafted polybutadiene samples. Assuming that branched chains are more easily destroyed than linear chains, it would be expected that both MA and MA-styrene grafted polybutadiene would exhibit reduced stability, commensurate with the amount of grafting. The introduction of tertiary carbon atoms on the chains should also facilitate kinetic chain transfer to polymer. Activation energy for this type of reaction is low, approximately 20.1 kcal/mol, and would be expected to cause a decrease in the average destruction energy.

Photoreactions of MA with 1,2-polybutadiene, 1,4-polybutadiene, poly(styrene-co-butadiene), poly(styrene-co-isoprene), polystyrene, and poly(styrene-co-methyl methacrylate) have been studied in air.<sup>(84)</sup> In homogeneous solutions, MA addition to the polymers proceeds efficiently by a chain mechanism, where the quantum yield of the photoaddition was greater than unity under irradiation at  $\lambda > 310$  nm. From the effects of solvent and photosensitizers and spectroscopic data, a radical chain mechanism was proposed to account for addition and crosslinking of the polymers by MA molecules.<sup>(84)</sup> The photoaddition reaction was applied to the surface of polymer films. The photoreactions were conducted at the interphase between solid polymer and acetone solution of anhydride and also at the interphase between solid polymer and gaseous anhydride. Irradiation with a 300-W high-pressure lamp brought about considerable surface modification, as shown by wettability and dyeability properties.

Mastication of polychloroprene with MA and MA–styrene or MA–vinyl acetate mixtures gives carboxylated chloroprene rubbers.<sup>(85)</sup> The extent of the mechanochemical grafting of the base polymer with anhydride is increased 3–4 times in the presence of the vinyl monomers. The results are akin to the case where styrene improves grafting of MA on polybutadiene.<sup>(47)</sup> Ivan *et al.*<sup>(196)</sup> have recently reported techniques for grafting MA on cyclopentadienylated polychloroprene.

Maleic anhydride has been grafted on polybutadiene and styrene–butadiene copolymers as a method to obtain improved coatings<sup>(86,153)</sup> and adhesives for glass fibers.<sup>(83)</sup> Treating low-molecular-weight styrene–butadiene copolymers with 1% anhydride for 2 h in refluxing xylene and subsequently hardening gave coatings with significantly improved adhesion. Reacting maleinized polybutadienes with dialkylaminoalkylamine provides useful waterborne coating resins.<sup>(153)</sup> The coating formulations were applied to metal surface by standard electrodeposition methods. Heating (200°C for 3 min) caused imidization, producing useful water-insoluble coatings.

Grafting of maleimide copolymers on conjugated diolefin elastomers has been discovered as a route to new molding resins with improved physical properties.<sup>(193)</sup> Low-molecular-weight polybutadiene, with substantial 1,2-microstructure, have also been heated with bismaleimides and peroxides to obtain grafted prepreg materials.<sup>(189,190)</sup> Composites prepared from these materials exhibit excellent high-frequency electrical properties, moisture resistance, dimensional stability, and shear strength.

#### 11.1.6. Other Unsaturated Copolymers

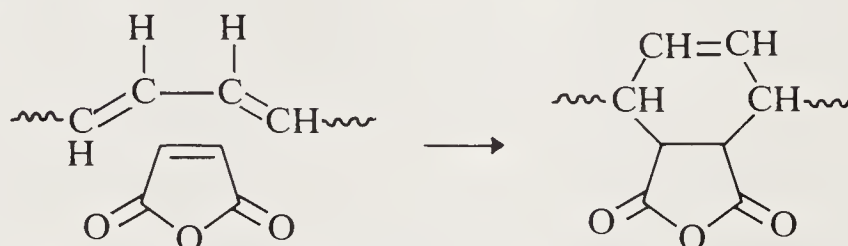
Ethylene–co–allene polymers, as prepared with  $(\text{iso-Bu})_3\text{Al-VCl}_3$  catalyst, have side-chain methylene, side-chain vinyl, in-chain *cis*, and in-chain *trans* unsaturation.<sup>(88)</sup> The side-chain methylene moiety appears to predominate in the copolymer. The copolymer is easily grafted with MA via the Diels–Alder reaction. Films of the grafted material, in comparison to ungrafted copolymer, exhibited greatly enhanced printability, due to the increased polarity. Polyallene has also been treated with MA and maleimides to obtain Diels–Alder type grafting and new polymers for possible use in coatings.<sup>(90)</sup> Little is known about the properties of these modified polymers and copolymers.

Polymers prepared from acetylene,<sup>(91)</sup> 1-hexyne,<sup>(92)</sup> phenylacetylene,<sup>(93–96)</sup> and derivatives of phenylacetylene<sup>(96,97)</sup> as well as acetylene–diene copolymers,<sup>(98)</sup> prepared by Ziegler-type catalysts, form adducts with MA. It is generally claimed that these maleinated products form by both Diels–Alder and ene-type reactions. However, there is some question about this conclusion for the acetylene homopolymer. Higashiura and Oiwa<sup>(91)</sup> claim the *trans–trans* polyene structure precludes the Diels–Alder reaction. Thus, they feel the MA copolymerizes with the double bond.<sup>(91)</sup> Other than



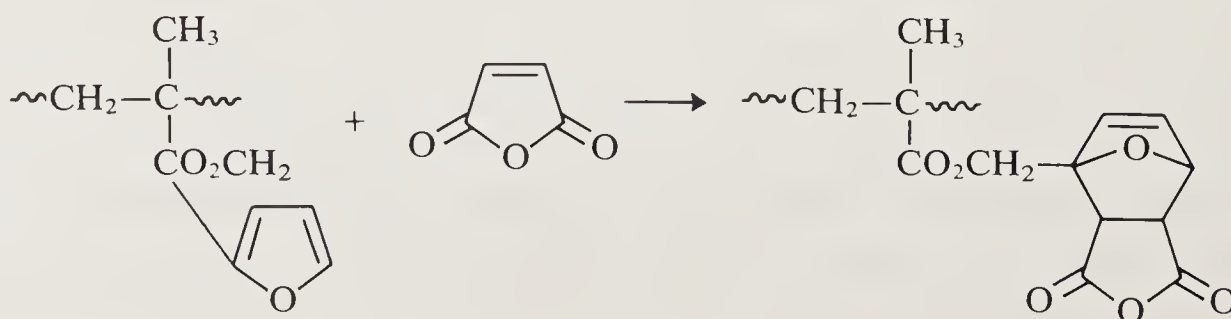
potentiometric titration, infrared, and semiconductor properties, little information is available on the properties of these modified acetylene polymers.<sup>(94,95)</sup> Ethylene-propylene-acetylene terpolymers have also been treated with MA.<sup>(99)</sup> Reactions in the melt readily produced terpolymer with grafted anhydride.

It is well known that MA has a stabilizing influence on poly(vinyl chloride) in the mill.<sup>(100-103)</sup> The presence of only 1–3% free MA inhibits thermal degradation of PVC. The effects of MA on the dehydrochlorination reaction of PVC has received substantial study.<sup>(104-110)</sup> Retardation of dehydrochlorination is attributed to the Diels-Alder reaction of MA with the conjugated polyene sequences formed, leading to improved color. Maleates and metal salts of maleic acid also perform as dienophiles for the stabilization reaction.<sup>(110)</sup> Previously dehydrochlorinated PVC, containing polyene regions, readily adds MA and dimethyl maleate at 40°C in tetrahydrofuran solvents,<sup>(171)</sup> but reaction rates are slow at room temperature. The isolated MA product showed the expected infrared absorption band at  $1780\text{ cm}^{-1}$  for carbonyl moieties. A plausible mechanism is shown as follows:



The surface of poly(tetrafluoroethylene) materials may be etched with potassium or liquid ammonia to produce double bonds.<sup>(113)</sup> These double bonds are usable as grafting sites for MA. Grafting is achieved with free-radical initiators, using neat polymerization conditions. Grafted tubes were tested for thrombogenic activity by exposure to animal blood. Thrombogenicity of the poly(tetrafluoroethylene) surface was improved, but carboxyl groups were inferior to sulfonic acid residues.

Polymers with pendent furfuryl residues readily undergo Diels-Alder reaction with MA and maleimides.<sup>(114,115)</sup> The polymers are potentially useful in ion-exchange resins and thermoset coatings. The poly(furfuryl methacrylate) or furfuryl methacrylate copolymers may be treated with MA to obtain a Diels-Alder product shown as follows:





Dehydration of poly(vinyl alcohol) fiber may be achieved in inert solvents with various inorganic dehydrating agents at 75–200°C. Conjugated double bonds are primarily formed during the reaction. MA readily grafts to such dehydrated fibers, via the well known Diels–Alder (see Chapter 4) reaction. The grafted materials are claimed to be useful as cation-exchange resins.<sup>(89)</sup>

#### 11.1.7. Carbon Black and Carbon Fiber Grafts

Fine-particle furnace blacks,<sup>(116)</sup> Nairit NT,<sup>(117)</sup> and carbon fibers<sup>(118,119)</sup> have been grafted with styrene-co-MA, vinyl acetate-co-MA, isoprene-co-MA, and other copolymers. Alternating styrene-co-MA and vinyl acetate-co-MA polymers are readily grown mechanochemically on the surface of carbon blacks.<sup>(116,117,120)</sup> The grafted materials have a strong tendency to gel, do not readily form dispersions, and increase the tensile strength and rigidity of rubber.

Carbon fibers treated with ozone ( $O_3$ ) and grafted with alternating isoprene-co-MA or styrene-co-MA have been shown to be excellent reinforcement materials for epoxy and polyester resins.<sup>(118,119)</sup> Products prepared with the grafted fibers exhibit improved shear strength, due to dampened fiber-matrix stresses. In the procedure, the carbon fibers were treated with moist air at 450°C or with air containing 5%  $O_3$  at 70°C and grafted with the copolymer in solution by  $\lambda$  irradiation. The shear strengths of the composites were increased by the carboxylated materials, due to dampened fiber-matrix stresses. Dioxane dispersions of carbon fibers have also been grafted with alternating styrene-co-MA polymer.<sup>(121)</sup> Again, the excellent adhesion provides epoxy resin composites with improved shear strength.

#### 11.1.8. Alternating Copolymer Grafts

Continuing from a previous section (11.1.5), where grafting of styrene-co-MA on polybutadiene was briefly discussed, alternating styrene-co-MA and other MA copolymers have been grafted on a variety of other polymeric materials.<sup>(45)</sup> These grafts may be prepared by conducting the copolymerizations of the donor and acceptor pairs (see Chapter 10) under conditions whereby alternating copolymers are formed, in the presence of substrate polymers containing tertiary or allylic C–H bonds.<sup>(122,123)</sup> The polymerizations may be carried out both neat and in solution, with solution giving the best yields. Initiators promote grafting but are only essential when the MA-comonomer pair will not spontaneously copolymerize. Inhibitors in polymers such as PVC fail to inhibit carboxylation.

Spontaneous, *in situ* bulk polymerization of styrene-MA in the presence of branched polyethylene,<sup>(36,122,124,125,129,133)</sup> polypropylene,<sup>(122,129,133)</sup> polystyrene,<sup>(122,127–129,133)</sup> poly(vinyl chloride),<sup>(122,133)</sup> poly(ethylene-co-

propylene),<sup>(133)</sup> poly(styrene-co-acrylonitrile),<sup>(130)</sup> *cis*-1,4-polybutadiene,<sup>(133)</sup> acrylonitrile-butadiene-styrene (ABS), and butadiene-acrylonitrile,<sup>(133)</sup> acrylic ester polymers and copolymers<sup>(122,126)</sup> have been investigated. The polymerizations may be carried out in a Brabender Plasticorder, screw extruder, or some other suitable mixing equipment, with the optimum temperature for reaction depending upon the softening or melting points of the substrate polymers.

When an equimolar mixture of styrene and MA, at 50–70°C, is injected into polyethylene, polypropylene, polystyrene, and others, at a temperature of 120°C, preferably at 150–200°C, polymerization is initiated and the growing chains terminate by insertion into the polymer.<sup>(134)</sup> It is claimed that activated complexes initiate the polymerization, but this is doubtful, since the styrene-MA complex fails to exist at the 120–150°C polymerization temperature (see Sec. 10.2.15). In most cases, due to temperature and dilution effects, the pendent alternating units are very short, i.e., 2–10 alternating units.<sup>(122)</sup> Low-density polyethylene because of the tertiary carbon atoms at branch points grafts much easier than high-density polyethylene, under comparable conditions.

Grafting on polypropylene clearly showed the effect of increasing the number of grafting sites and decreasing the substrate polymer melt viscosities. Grafting equimolar styrene-co-MA in solution on polypropylene, by free-radical initiators, has also been disclosed in the patent literature.<sup>(131)</sup> Carboxylation of atactic polypropylene requires a temperature of 150°C. In contrast, effective carboxylation of isotactic polypropylene requires a temperature of at least 170°C. Analogous to PVC, polypropylene grafting reactions were not subject to conventional inhibitors and normal additives in the commercial polymer failed to interfere with the reaction.

Isoprene-MA alternating copolymers may also be grafted on polystyrene both in solution<sup>(122)</sup> and a Brabender Plasticorder.<sup>(129,133)</sup> Grafting goes best in dioxone solvent at 65–75°C, using peroxide initiators. Without peroxide initiators, the isoprene-MA mixture gives substantial Diels-Alder product (see Chapter 4).

Polypropylene fiber has been exposed to a 2-MeV electron beam and subsequently treated with a styrene-MA monomer mixture to obtain grafted fiber.<sup>(135,136)</sup> Vinyl acetate-co-MA grafting of the polypropylene fibers was also achieved. Grafting improved the dyeability and heat resistance of the fiber.

Polyethylene, polypropylene, and Teflon films undergo graft copolymerization, using vapor-phase grafting techniques.<sup>(137)</sup> Polyethylene film, exposed to  $\gamma$  radiation (<sup>60</sup>Co) at dose rates of  $2.0\text{--}3.5 \times 10^4$  R/h and UV light from an ultrahigh-pressure mercury lamp at 25°C and various donor-acceptor monomer mixtures, was grafted with indene-co-MA,<sup>(138)</sup> acenaphthylene-co-MA and 1,1-diphenylethylene-co-MA alternating copolymer. The grafting degree for the indene and acenaphthylene substrates were 35.4 and 29.0%,



respectively. Butadiene polymer films, exposed to UV at 30°C, have also been grafted with MA vapor.<sup>(139)</sup>

The patent literature discloses that anionically prepared butadiene-co-styrene block copolymers may be grafted with alternating styrene-co-MA copolymer.<sup>(132)</sup> Grafting is best achieved in aromatic solvents, with styrene/MA mixtures and peroxide initiators for 4 h at 80°C, to give dioxane-soluble materials. These grafting procedures were explored as routes to new elastomers. A recent patent<sup>(161)</sup> discloses that polyblends consisting of styrene-MA grafted SBR50, ABS, and acrylonitrile-co- $\alpha$ -methylstyrene polymer provide moldings with improved heat distortion. For example, one polyblend exhibited heat distortion of 106°C at 18.6 kg/cm<sup>3</sup> stress, Izod impact strength (2.54-mm notch) of  $1.73 \times 10^{-2}$  J/m, and falling dart impact strength of 61.0 J.

Alternating propylene-co-MA and styrene-co-MA residues have been grafted to ethylene-co-vinyl acetate polymer, using free-radical initiators in benzene solution at 85°C.<sup>(37)</sup> The resultant anhydride grafted materials were shown useful for preparing composites and molded objects with improved physical properties.<sup>(39)</sup>

Using preozonization techniques for activation, alternating styrene-co-MA has been grafted on poly(ethyl acrylate) and poly(ethyl acrylate) grafted on the alternating styrene-co-MA substrate.<sup>(140-142)</sup> The solution, solid state, glass transition temperature, dielectric relaxation, and other properties of the materials were studied. It was shown that such graft copolymers exhibit original properties depending sometimes on the nature of the grafted chains and due to the miscibility of the two polymeric moieties.

The above approach has also been explored for preparing poly(vinyl chloride) (PVC) grafted with styrene-co-MA and alternating styrene-co-MA polymer grafted with PVC.<sup>(142)</sup> For each type of graft copolymer a series of homogeneous products can be obtained, varying in composition between those having a few long branches and those having many short ones. This distribution factor corresponds to the topochemical structure of the materials. Thus, each graft copolymer is characterized by three elements: the chemical composition, the type of grafting, and the topochemical structure. The influence of these three variables on rheological properties were examined. The particular properties examined were glass transition points, as measured by the changes of rigidity modulus and the melt flow, and the variation of this melt flow with temperature. The second-order transition point ( $T_g$ ) was shown to be a function of the composition, being higher for long side grafts and independent of the way of grafting. The  $T_g$  also increased with the styrene-MA content and was similar for both systems with the same composition. Blends of PVC and the styrene-MA copolymer are incompatible, exhibiting the normal PVC  $T_g$ . The melt viscosity was a function of the grafting length. This system is probably comparable to what would happen in many other grafting systems, at least in a qualitative sense.



Knowing that esterification of cotton by MA gives improved soil release and wash-fast properties, alternating styrene-co-MA grafting on cotton has been studied as a way to also improve soil-release properties.<sup>(143)</sup> However, grafting did not give the desired improvement.

Grafting of styrene-co-MA on soft tissues such as collagen, in the presence of ceric ions, persulfate-bisulfite, or zinc chloride, has been examined as a way to modify the surface properties of materials such as ratskin or calfskin.<sup>(144)</sup> The surface grafting results in changes in the wettability and water absorption of the substrates. Modified hydrophilic, hydrophobic, and oil-repellent surfaces could be prepared. The treated surfaces were also more resistant to fungal attack. Wool fiber has also been vinylated and grafted with MA and maleimides, both with and without swelling solvents, to change surface properties.<sup>(145)</sup> Without solvents only surface grafting was achieved; with swelling solvents, grafting occurred throughout the fiber. Wettability, shrink resistance, hand, and other properties were modified by both the type and extent of grafting.

Styrene-co-MA has been converted to a partial perester in acetone solution, using *tert*-butyl hydroperoxide and pyridine catalyst.<sup>(146)</sup> The partial peresters were used to initiate methyl methacrylate polymerization by a thermal mechanism in a homogeneous acetone solution. The method provided both homopolymer and graft copolymer. Grafting of methyl methacrylate or styrene-co-MA was also achieved with *tert*-butyl hydroperoxide initiator. However, grafting by transfer was substantially less than grafting by the perester technique. Partially neutralized styrene-co-MA has also grafted with acrylonitrile in aqueous solution by a redox initiation procedure.

## 11.2. GRAFT COPOLYMER USES

As shown in the comprehensive patent listing (Table A.7) and briefly mentioned in previous sections, polymeric materials with pendent MA or MA copolymer grafts are claimed to have wide possible uses. As pointed out earlier, MA grafting provides enhanced polarity and functionality on polymeric substrates. These two added features are readily exploited, in a variety of ways, to prepare new products.

In the coatings area, the carboxylated resins are useful for preparing waterborne, corrosion-resistant metal primers and can coatings, with good gloss, solvent resistance, adhesion, and impact properties.<sup>(76)</sup> Abrasion-resistant coatings applied by the electrodeposition techniques are also possible. Glossy paper coatings, for applications such as milk cartons, floor polishes or waxes, and sizing for textile fiber are also possible. Maleinated materials are also useful as modifiers for air-drying alkyds, as masonry and clay particle coatings, and for improving both compatibility and curing speed for various

coating systems.<sup>(56)</sup> Grafted materials are unique modifiers and hardeners (crosslinkers) for epoxy resin coatings and adhesives. Maleinated resins may also be useful in coatings as emulsifiers or dispersants for latex dispersions.

Primary amine derivatives of the MA-grafted material, such as MA-grafted polyolefins, may be converted to maleimide grafts. This generally improves the impact and heat distortion temperature of plastics, with no sacrifice in transparency, soil release, and other properties.

Allyl derivatives of maleinated materials are useful in photocurable systems and as modifiers for unsaturated polyester resins. In both uses, the allyl residues are utilized in crosslinking reactions, providing thermosets with improved hardness, solvent resistance, heat resistance, and other properties.

Rubbers may be grafted to obtain materials with improved green strength, tensile strength and modulus, reduced cold flow, and improved tack properties. In rubber composites, grafting may provide improved impact properties. Improved tire tread rubbers have been prepared. Rubbers may be prepared that can be vulcanized without the use of sulfur, using weak acid metal salts and moisture curing. MA-modified rubbers have not found any substantial use, however, possibly because processing on a large scale is unsatisfactory. Dinges<sup>(172)</sup> recently discussed possibilities and limitations in the synthesis of a new rubber from conventional rubber by treatment with MA. Ethylene-propylene-diene elastomers have improved vulcanization properties and become potentially useful materials after grafting. Maleinated materials have given improved rubber adhesives, rubber tackifiers and function well as a dispersant for rubber latex emulsions. Allyl derivatives of maleinated rubbers are also useful materials, curable with peroxide initiators and other crosslinkers to give thermoplastic elastomers. A recent patent<sup>(150)</sup> claims that MA-grafted diene-based elastomers partially neutralized with tertiary alkyl amines exhibit unique properties. The products behave like vulcanized elastomers at 0–100°C but are free-flowing molten thermoplastics at around 150°C with easy-processing properties.

In the fibers and films area, MA grafting provides polyolefins with highly improved dyeability, adhesion, and moisture regaining properties. Nylon-grafted materials also exhibit much improved wettability properties. It is also known that isotactic polypropylene-Nylon 6 blends may be prepared with a propylene-MA copolymer additive promoting compatibility.<sup>(149)</sup> Grafted polyolefins are potentially useful in sealable packaging films. Hot melt adhesives, glass fiber coatings to improve adhesion in plastic laminates, metal-polyolefin laminate adhesives, metal-polyolefin and nylon-polyolefin adhesives, as well as others, are obtainable from MA-grafted materials. Grafted materials are also useful extrusion aids for a variety of polyolefins. A recent patent<sup>(151)</sup> describes in good detail how MA grafting significantly affects the adhesion of polyolefins to polar polymer substrates.



Rigid PVC foams may be produced by mixing PVC, MA, vinyl comonomers, free-radical initiators, and diisocyanates and heating the mixture in a mold under pressure.<sup>(147)</sup> Grafting occurs during the reaction. The flexible, gelled product may be exposed to water or steam to obtain the desired foam.<sup>(112,117)</sup> The CO<sub>2</sub> formed acts as a blowing agent and the density of the foam is controlled by diisocyanate content. Such materials are useful in lightweight structural applications.

Many other possible uses have also been claimed in the moldings and laminates, PVC additives, printing inks, paper sizing, ion exchange, soil stabilization, cellular materials, adhesives, lubricant additives, reinforced thermoplastics, aluminum–paper laminates, polyolefin ionic crosslinking, and extruded polyolefin areas for MA-grafted materials. Despite the great amount of MA grafting work, most of which is disclosed in the patent literature (Table A.7), and obvious potential uses for such materials, very little market volume has developed for MA in grafted polymeric materials. Perhaps this will change in the future, as grafting is more explored and exploited to prepare polymers better tailored to meet specific needs.



# 12

## MALEIC ANHYDRIDE IN CONDENSATION POLYMERS

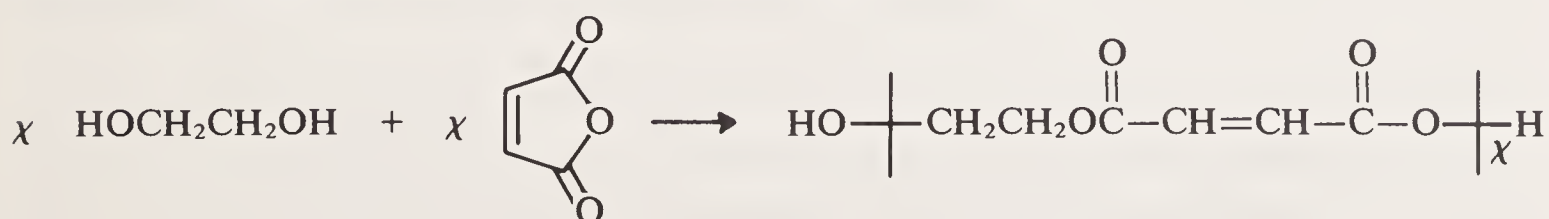
### 12.1. INTRODUCTION

When considering the use of MA in condensation polymers, it is automatic to think of unsaturated polyesters. In fact, the demand for MA is keyed primarily to the growth of these resins. In 1980, about 172 MM lb of MA were used to produce polyester resins in the United States.<sup>(1)</sup> This represented approximately 52% of the 330 MM lb of MA demand in the United States in 1980 (see Sec. 1.4.1). MA is also very useful in other condensation polymers, including about 6 MM lb in alkyd resins.<sup>(2-4)</sup> The value of using MA to prepare, crosslink, and/or modify condensation and addition polymers is discussed in this chapter. In recent times, the synthesis of maleinated vinyl esters and maleimide resins have had significant study. Because of this interest, we also give some attention to the use of MA in vinyl ester and maleimide technology.

### 12.2. UNSATURATED POLYESTERS

#### 12.2.1. Introduction

Unsaturated polyesters are based on macromolecules with a polyester backbone in which an unsaturated acid or combination of a saturated with an unsaturated acid are condensed with a glycol. A three-dimensional structure is produced when the macromolecule is crosslinked through the unsaturation. Commercial unsaturated polyester resin formulations, neglecting consideration of additives, initiators, extenders, and fibrous reinforcing materials, consist essentially of a linear resin, a crosslinking (reactive diluent) monomer (ca. 18–40 wt. %), and inhibitors to retard crosslinking until the resin is used by the fabricator. The simplest member of the polyester series, ethylene maleate (or ethylene fumarate), is prepared as follows:



Saturated dibasic acids are commonly employed with the unsaturated acid to modify the degree of unsaturation and thereby the reactivity of the resulting polyester. Muskat<sup>(5)</sup> showed that the inclusion of phthalic anhydride into the polyester formulation reduced the tendency of the resin to crystallize and improved the compatibility of the resin with styrene.

In addition to MA, phthalic anhydride, and ethylene glycol, other common intermediates used for the production of unsaturated polyesters are fumaric acid, isophthalic acid, adipic acid, propylene glycol, diethylene glycol, and dipropylene glycol. Table 12.1 provides a summary of both common and specialty building blocks used in polyesters and contributions made by these intermediates to the properties of the products. Recycled polyethylene terephthalate beverage bottles may one day become an important raw material for unsaturated polyester resin production, providing an alternative for a substantial part of the petroleum-based intermediates.<sup>(1008)</sup>

Unsaturated polyesters prepared from the intermediates in Table 12.1, formulated with various vinyl-type unsaturated monomers such as styrene, have been widely studied, patented, and discussed in the literature.<sup>(6,7)</sup> Bjorksten's<sup>(8)</sup> book gives a good presentation of the early studies on the chemistry, production, and applications of unsaturated polyesters.

## 12.2.2. Production

### 12.2.2.1. Glycol–Anhydride Reactions

Over the years many studies have looked at ways to reduce the processing time for the production of unsaturated polyesters.<sup>(9)</sup> Normally, the resins are usually prepared at 210–225°C. The polycondensation rates are dependent upon the structures and the ratio of the reactants,<sup>(10,11)</sup> with third-order kinetics observed.<sup>(12,13)</sup> The number average degree of polymerization (DP) is almost proportional to the square root of the time, for a third-order condensation. Although low-molecular-weight oligomers form rapidly, the rate of increase of molecular weight with time decreases as the third-order reaction proceeds, and the attainment of high molecular weight requires long reaction time. The velocity of the polycondensation reaction is strongly dependent on the presence and nature of esterification catalysts.<sup>(14)</sup> The necessity for the use of catalysts and their nature also varies markedly with the polyester intermediates. Depending on the choice of starting materials, unsaturated polyester resins are generally fairly linear, with molecular weights ranging between about 700 and 5 000 and acid number around 40.<sup>(15,16)</sup> To drop the acid number to the 0–10 range requires catalysts. Recommended catalysts include tetrabutyl titanate, tetrabutyl zirconate, zirconium naphthenate, and mixtures of stannous oxalate and sodium acetate.<sup>(14)</sup> Tin compounds such as stannous chloride, stannic chloride, dibutyltin oxide, and tributyltin hydroxide are also recommended.<sup>(17)</sup>



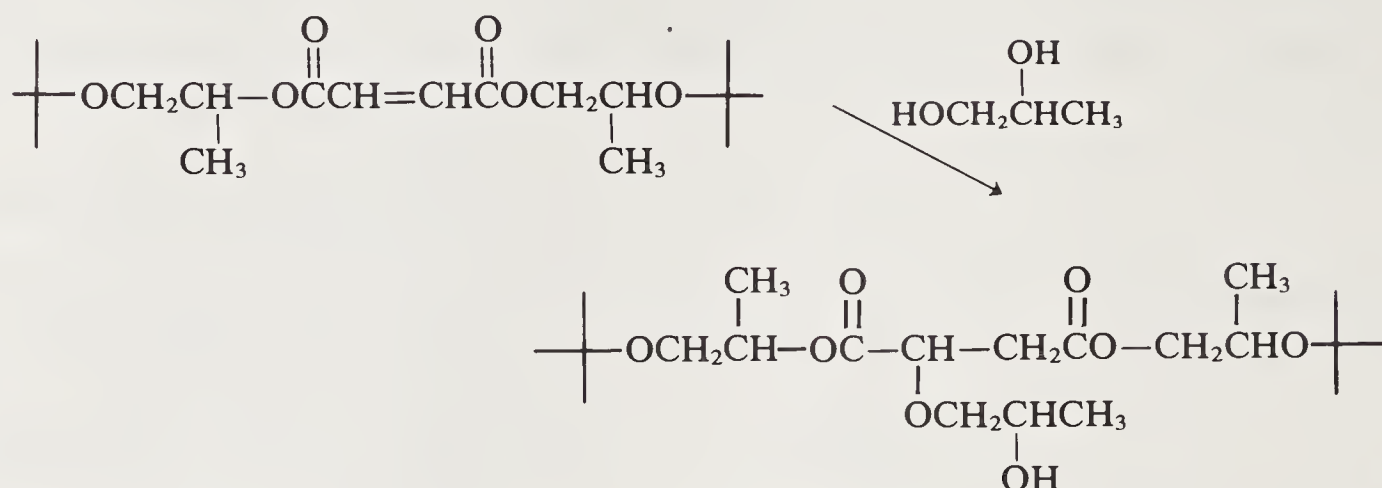
Table 12.1. Unsaturated Polyester Building Blocks

Building Blocks	Ingredients		Characteristics	
Unsaturated anhydrides and dibasic acids	a.	Maleic anhydride	a.	Lowest cost, moderately high heat deflection temperature (HDT)
	b.	Fumaric acid	b.	Highest reactivity (crosslinking), higher HDT, more rigidity
Saturated anhydrides	a.	Phthalic ( <i>ortho</i> -phthalic) anhydride	a.	Lowest cost, moderately high HDT, provides stiffness, high flex, and tensile strength
	b.	Isophthalic	b.	Higher tensile and flex strength, better chemical and water resistance
	c.	Adipic acid, azelaic acid, and sebacic acid	c.	Flexibility (toughness, resilience, impact strength); adipic acid is lowest in cost of flexibilizing acids
	d.	Chlorendic anhydride HET anhydridel	d.	Flame retardance
	e.	Nadic methyl anhydride	e.	Very high HDT
	f.	Tetrachlorophthalic anhydride	f.	Flame retardance
	g.	Tetrabromophthalic anhydride	g.	Flame retardance
Glycols	a.	Propylene glycol	a.	Lowest cost, good water resistance and flexibility, compatibility with styrene
	b.	Dipropylene glycol	b.	Flexibility and toughness
	c.	Ethylene glycol	c.	High heat resistance, tensile strength, low cost
	d.	Diethylene glycol	d.	Greater toughness, impact strength and flexibility
	e.	2,2,4-Trimethyl-1,3-pentanediol glycol	e.	Corrosion resistance with reduced density
	f.	Bisphenol-A adduct	f.	Corrosion resistance, high HDT, high flex and tensile strength
	g.	Hydrogenated bisphenol-A adduct	g.	Corrosion resistance, high HDT, high flex and tensile strength
	h.	Tetrabromo bisphenol-A	h.	Flame resistance

There is evidence in the literature<sup>(12,18)</sup> that long-term, high-temperature production procedures bring about branching of the propylene glycol-MA resins. Other side reactions have also been detected and studied.<sup>(20)</sup> The branching of polyester resins has been attributed to addition of the glycol to



the maleic double bond, bringing about a 15% reduction of double-bond availability.<sup>(21)</sup> The reaction is pictured as follows:



#### 12.2.2.2. Epoxide–Anhydride Reactions

Unsaturated polyesters may also be prepared by copolymerizing mixtures of cyclic ethers and anhydrides.<sup>(22–29,1014,1047,1133)</sup> This method has the advantages of a much faster reaction than using glycols and starting materials such as ethylene oxide or propylene oxide that are cheaper on a mole basis than the corresponding glycols. It is necessary to use a small amount of a glycol or acid to initiate the cyclic ether–anhydride reaction. If the initiating material is a glycol, the glycol reacts with the anhydride to produce monoester. The carboxylic acid residue of the monoester, in the presence of catalyst, reacts with the cyclic ether to regenerate the hydroxyl group. Molecular weights of the polyesters are controlled by the quantity of initiating glycol used. As solvating agents, glycols also speed up the propylene oxide–MA reaction.<sup>(1013)</sup> A probabilistic model for the propylene oxide, MA, and phthalic anhydride reaction, with propylene glycol initiator, was recently proposed and confirmed.<sup>(30)</sup> Measurement of the heat of polymerization of various epoxides, MA, and phthalic anhydride combinations show rates of polymerization are favorable for industrial applications at 120–220°C.<sup>(444)</sup> A large number of acids, bases, and salts have been studied and patented as catalysts for the reaction. Two catalysts that have received substantial attention are lithium chloride<sup>(22,23)</sup> and zinc chloride.<sup>(25)</sup> Lithium chloride catalyses only the polyesterification reaction, whereas, zinc chloride catalyses both polyesterification and polyetherification. A recent study of various organic substituted zinc catalysts showed that an increase in the acidity of the zinc atom favors a copolymer with lower degree of alternation, more propylene oxide units, and lower molecular weight.<sup>(1015,1140)</sup> With the zinc chloride catalyst it is necessary to use a large excess of cyclic ether to reduce the acid number of the polyester to the desired level. The resulting unsaturated polyester contains, in the case of the propylene oxide–MA starting material, not only propylene units but dipropylene units in the polymer backbone. The resulting resin, due to

dipropylene glycol residues, would be more flexible than the corresponding resin prepared from propylene glycol and MA.

Disadvantages of the cyclic ether procedures for preparing unsaturated polyesters include reduction of the latitude for resin compositions, difficulty of obtaining low-odor, low-color materials, and need of a second step to isomerize the resins. However, excellent low-cost general purpose polyester resins may be prepared by this route, as shown by the patent literature. Side reactions in the catalytic isomerization of unsaturated polyesters and a mathematical model of the process has been studied by Klyuchnikov *et al.*<sup>(1138)</sup> using piperidine catalyst. Carpenter and Peterson<sup>(31)</sup> recognized the potential and developed a high-pressure process for the continuous production of unsaturated polyesters from the epoxide–anhydride reaction. Exercising the claims of the patent,<sup>(31)</sup> Ashland Chemical Company has a plant to continuously produce general purpose unsaturated polyester resins. Carpenter<sup>(1007)</sup> recently discussed advantages and limitations of the continuous unsaturated polyester production procedure.

Deanin and Dossi<sup>(32)</sup> used the propylene oxide–MA reaction to prepare cured polyester resin products in a one-step procedure. In the method explored, the epoxide, MA, phthalic anhydride, styrene, lithium bromide, and benzoyl peroxide were combined, heated to a melt, and cured as castings. The properties of the cured materials were inferior to conventional systems. Others have also studied this concept.<sup>(33)</sup> A one-step (condensation–addition) polymerization procedure has also been studied as a method for preparing coatings<sup>(245)</sup> and laminates with epoxy resins.<sup>(34–37)</sup>

In addition to ethylene and propylene oxide, a variety of other cyclic ethers have also been copolymerized with MA. Monomers such as cyclohexene oxide,<sup>(38)</sup> piperylene dimer mono and diepoxide,<sup>(39)</sup> epichlorohydrin,<sup>(40–42)</sup> 3,3,3-trichloropropylene oxide,<sup>(43)</sup> tetrahydrofuran,<sup>(44)</sup> and ethylene carbonate or ethylene sulfite<sup>(45)</sup> have received attention. Condensation reactions between allyl glycidyl ether and MA are reported to be highly useful for preparing plastics with remarkable hardness, high heat distortion, and brilliant clarity.<sup>(46)</sup> The cyclohexene oxide copolymerizations were second order in MA, with an activation energy of 13.8 kcal/mol. For the epichlorohydrin system the rate was dependent on the temperature and proportional to the catalyst concentration, with an activation energy of 14.5 kcal/mol.

### 12.2.3. Maleate–Fumarate Isomerization

Maleate-containing polyesters are difficult to prepare and they copolymerize sluggishly with conventional monomers such as styrene. In contrast, fumarates copolymerize rapidly with styrene.<sup>(19)</sup> Thus, it is very fortunate that conventional polyesterification procedures lead to substantial isomerization of maleate to fumarate residues. In cases where the optimum physical properties are demanded and nonobtainable from the incompletely isomerized



polyester, the needed resin may be prepared from fumaric acid. The fumarate residue contributes greater hardness, higher heat distortion, and greater shrinkage for the cured materials and higher viscosities and longer pot life for the uncured resins. These properties can all be contributed to greater crosslinking for the fumarates.

Several studies have been centered on developing the kinetics,<sup>(48)</sup> understanding the mechanism,<sup>(49-51)</sup> and finding catalysts to promote the isomerization of maleates to fumarates.<sup>(52,53)</sup> Isomerization has been studied by the use of infrared analysis, polarographic techniques,<sup>(54,55)</sup> and nuclear magnetic resonance (NMR) analysis.<sup>(50,56)</sup> The NMR method, used for the results in Table 12.2, is considered best. The results in Table 12.2 show that the percentage of fumarate moieties increase as the glycol becomes more sterically hindered.<sup>(50)</sup> Isomerization is also increased by the presence of aromatic dibasic acids. As the polyesterification temperature is increased the isomerization also increases. However, changing the esterification temperature does not affect the total amount of isomerization occurring over the range of temperatures studied.<sup>(7)</sup>

Unsaturated polyester resins prepared from epoxides and MA are usually conducted in a manner which gives only the maleate copolymer.<sup>(23)</sup> This necessitates heating the resin for several hours at 200°C, to bring about the needed maleate-fumarate isomerization. The isomerization may be facilitated by a variety of catalysts, reducing both the temperature and time needed to

Table 12.2. Maleate to Fumarate Isomerization During Polyesterification<sup>a</sup>

Glycol Used	Saturated acid <sup>b</sup>	% Fumarate
Cyclohexanedimethanol	—	33
Diethylene	—	50
Neopentyl	—	50
Ethylene	—	75
Propylene	—	93
2,2,4-Trimethyl-1,3-pentanediol	—	93
Cyclohexane dimethanol	PA	52
Diethylene	PA	52
Neopentyl	PA	85
Ethylene	PA	84
Propylene	PA	94
Diethylene	IPA	65
Neopentyl	IPA	72
Ethylene	IPA	71
2,2,4-Trimethyl-1,3-pentanediol	IPA	96
Propylene	IPA	95

<sup>a</sup> Reprinted with permission from *Indus. Eng. Chem. Prod. Res. Dev.* 3 (3), 218 (1964). Copyright © 1964, American Chemical Society.

<sup>b</sup> PA = phthalic anhydride; IPA = isophthalic acid.



achieve the desired fumarate content. The kinetics of the first-order isomerization reaction has been studied in great detail using piperdine catalyst.<sup>(24)</sup> Nuclear magnetic resonance, using the <sup>13</sup>C technique, has been shown to be very useful for structural analysis of the polyesters prepared from epoxides.<sup>(57)</sup>

12.2.4. Reactive Diluent Monomers

As pointed out in the introduction, unsaturated polyester resins are commonly combined with reactive diluent monomers (Table 12.3). Styrene is most frequently used for this purpose.<sup>(58-62)</sup> However, monomers such as methyl methacrylate,<sup>(63,64)</sup> diallyl phthalate,<sup>(60,65-70)</sup> triallyl cyanurate,<sup>(60-70)</sup> vinyl toluene,<sup>(60,71)</sup>  $\alpha$ -methylstyrene,<sup>(60)</sup> *p*-*tert*-butylstyrene,<sup>(72)</sup> and chlorostyrene<sup>(60,73)</sup> have also been studied (Table 12.3), showing varying degrees of utility.

Table 12.3. Monomers Used in Unsaturated Polyester Systems<sup>a</sup>

Monomer	Boiling point (°C)	Volume shrinkage (%)	Characteristics
Styrene	145	15	Low cost, high reactivity, fairly good heat distortion temperature, high flex strength
Vinyl toluene	171	12.5	Reduced volatility and shrinkage, high reactivity, more flexibility
Chlorostyrene	187	12	Reduced volatility, low shrinkage and fast coreaction
$\alpha$ -Methylstyrene	166	—	Control of exothermic heat
<i>p</i> - <i>Tert</i> -butylstyrene	219	7	Very low shrinkage and low volatility
Divinylbenzene	195	—	Extra crosslinking
Diallyl phthalate	290	18	Very low volatility, fast cure, long shelf life, high heat resistance
Triallyl cyanurate	162	—	Improved heat resistance, high reactivity, high flex and tensile strength
Methyl methacrylate	100	20	Improved weathering, good translucency properties, fairly high heat distortion

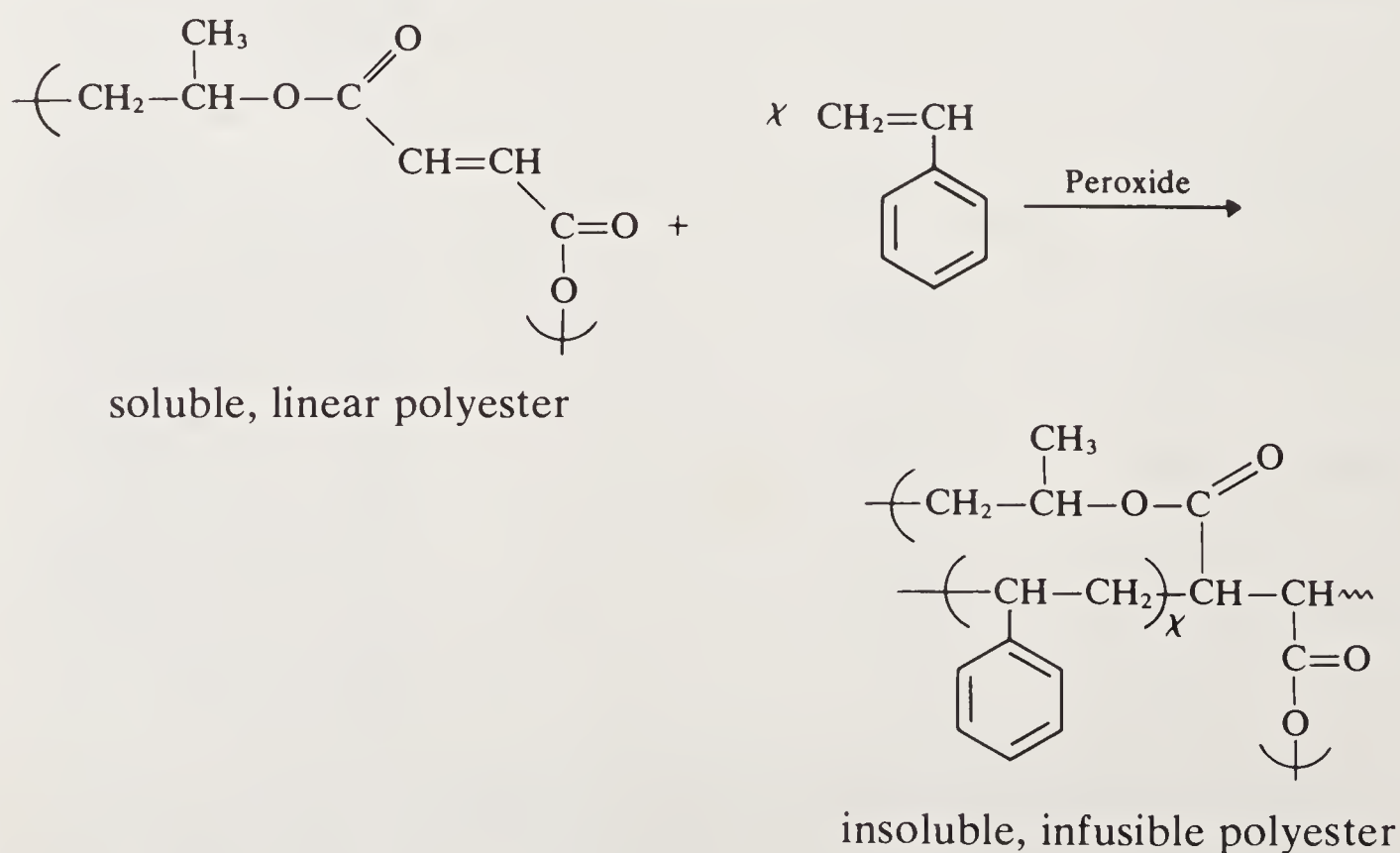
<sup>a</sup> Other monomers that have been evaluated or used to some extent to gain special properties include vinyl acetate, ethyl acrylate, 2-ethylhexyl acrylate, 2-vinyl pyridine, *n*-vinyl pyrrolidone, dichlorostyrene,<sup>(62,74)</sup> and bromostyrene.<sup>(75)</sup>

The ideal reactive diluent should be a low-cost, high boiling liquid with high but controllable reactivity for crosslinking. In some cases, the monomer should also exhibit low shrinkage on curing, such as given by *p*-*tert*-butylstyrene.<sup>(72)</sup> Maleimides have also been employed in combination with other vinyl monomers to improve the toughening and heat resistance of the cured resins (Sec. 12.2.7).<sup>(76)</sup> It has been clearly shown that the microstructure of the cured resins is a function of the nature of the monomers and the preparative procedures.<sup>(77)</sup> It is interesting to note, there have been a few cases mentioned in the literature where MA has been used as a free monomer to crosslink unsaturated resin systems. In one example, *p*-isopropenylphenol-formaldehyde resins were crosslinked with MA, using peroxide initiation, to give composite materials that did not melt up to their decomposition temperature.<sup>(78)</sup>

Unsaturated polyester-acrylic acid mixtures have been polymerized *in situ* on polyester fibers to provide graft polymer sizes that are easily removed by neutralization with a base.<sup>(1063)</sup> This type of combination has also been claimed for producing photopolymerized printing plates.<sup>(1064)</sup> These two patents give examples of how unsaturated polyesters may be mixed and polymerized with unconventional reactive diluent monomers to meet new special needs.

### 12.2.5. Crosslinking Reaction

The structure of unsaturated polyester crosslinking with vinyl monomers, such as styrene, may be described in the simplest form as short polystyrene units linked by double bonds at different polyester molecules, as follows:





The final crosslinked structure depends upon the extent of maleate to fumarate isomerization (Sec. 12.2.3), the level of unsaturation in the resins, the ratio of vinyl monomer to polyester, the number and type of unsaturated residues in the polyester chain, the steric and electronic effects of the acid and glycol residues in the polyester, and the initiator type and level. Many approaches have been developed to predict and elucidate the structure of cured polyesters<sup>(79-93)</sup> and determine the various acids and glycol residues.<sup>(95-101)</sup> There are usually about three polymerized styrene units between reacted fumarate moieties, showing that the polymerized vinyl monomer-unsaturated polyester is a very dense network structure. Maleate double bonds show only limited participation in the crosslinking reaction. A small percentage (3-7%) of unsaturated groups usually remain unreacted and very little free polystyrene is ever present in most cured systems.<sup>(94)</sup> Polystyrene is formed in cases where the styrene/fumarate ratio is greater than 9:1. For very low levels of styrene there is some indication that fumarate-fumarate crosslinking may also occur.<sup>(88,89)</sup>

Considerable effort has been expended to understand and control the crosslinking of polyesters,<sup>(102-109)</sup> and determine kinetics,<sup>(110)</sup> gel effect,<sup>(112)</sup> and the crosslinking mechanism.<sup>(88,111,113-132)</sup> In many cases the crosslinking information was obtained by chemical studies of the alkaline degradation products of the polyester networks.<sup>(128-132)</sup> Kinetic studies of the cure rate are very difficult, since gelation occurs by the time the reaction has progressed to only about 1-2%.<sup>(110)</sup> The early onset of crosslinking enhances the gel effect and the decreasing mobility of the growing chains causes a decrease of the termination rate constant. This brings about a net increase in free-radical concentration, leading to an exponential increase in the rate of monomer consumption. Gelation time decreases exponentially with the absolute temperature.<sup>(128)</sup> The activation energy of gelation, shown for one case, was about 24.3 kcal/mol.<sup>(128)</sup> Heat of copolymerization ( $\Delta H_{\text{cop}}$ ) studies,<sup>(133)</sup> expressed as the excess in comparison to the heat of polymerization of styrene present in the resin, is an increasing function of the ratio of unsaturated polyester to styrene, with a maximum at a 1:1 molar ratio. The measurement of the exotherm and time to peak temperature provides a means of observing the gel effect and comparing resin reactivity.<sup>(112)</sup>

The heats of reaction and kinetics of a general purpose thermoset polyester were very recently investigated by using differential scanning calorimetry techniques.<sup>(134)</sup> The heats of reaction, at different curing temperatures, and a kinetic expression of the crosslinking reaction were developed and compared to results of other studies. The proposed kinetic model could be utilized to obtain the rates of heat generation and the extent of cure at different cure temperatures and time. The overall activation energy of the curing reaction was estimated on the basis of the experimental data as 12.0 kcal/mol and the overall reaction rate constant as  $2.70 \times 10^9 \exp(-17,000/RT) \text{ min}^{-1}$ .



There is a need to know when the optimum properties of a cured system are obtained. Undercured resins are inferior and too long a cure schedule is uneconomical, so monitoring the degree of cure is very important in polyester curing steps. Kaminski<sup>(1009)</sup> recently described how ultrasonic viscometry may be used as a tool to study the relationship between viscosity of the resin and its gel time. The simple technique of measuring hardness as cure progresses appears to suffice for general use.<sup>(135,136)</sup>

### 12.2.6. Crosslinking Initiation

Initiators are needed to bring about the polymerization (curing) of unsaturated polyester resin–vinyl monomer mixture, to give infusible materials. As shown in Sec. 12.2.5, peroxides or hydroperoxides are commonly employed as a source of free radicals for initiation.<sup>(137–149)</sup> Free radicals are formed by thermal decomposition of the initiators during press molding applications, or by chemical decomposition in ambient (room temperature) curing applications. Cumene hydroperoxide, methyl ethyl ketone peroxide, and hydrogen peroxide are most widely used for ambient curing systems, whereas benzoyl peroxide is the most popular for medium-temperature curing.<sup>(150)</sup> Tertiary butyl perbenzoate and dicumyl peroxide are often used in molding operations, requiring temperatures on the order of 150°C.

Unsaturated polyester–vinyl monomer systems often require or utilize complicated initiator–accelerator–inhibitor combinations to provide optimum cure–stability profiles.<sup>(150)</sup> The accelerator is a compound that reacts with the peroxide initiator to generate free radicals at a lower temperature than would be the case in the absence of the accelerator. A wide variety of activators or accelerators have been evaluated and are available for ambient curing of unsaturated polyesters.<sup>(111,150–165)</sup> The combination of methyl ethyl ketone peroxide and cobalt octoate or benzoyl peroxide and *N,N*-dimethylaniline are particularly effective, commonly employed initiator–accelerator combinations. Of all the combinations studied, the benzoyl peroxide–dialkylaniline pair is probably best for obtaining the most complete cure at room temperature.

Inhibitors, which are added in ppm concentrations, are extremely important additives for unsaturated polyester–vinyl monomer mixtures.<sup>(166–171)</sup> Without inhibitors styrene–unsaturated polyester resin blends will slowly polymerize at room temperature and the ensuing heat of the exothermic reaction could actually cause an explosion of a large resin mass. The inhibitors provide good shelf life, inhibit premature gelation, reduce the peak exotherm, and prevent undesirable manifestations such as cracks in the formed articles. Other benefits, such as resistance to inhibition or acceleration of gel times in the presence of other additives, resistance to discoloration during processing, and resistance to gel time drift during storage of both catalyzed and

uncatalyzed systems may be obtained. In effect, the handling properties of unsaturated polyester resin mixtures depend greatly upon the inhibitor(s) employed.

Initiation of unsaturated polyester resin polymerization by electron beam,  $\gamma$  radiation,<sup>(172–187,441)</sup> and UV light<sup>(188–190,446,1035,1064,1066)</sup> has also received considerable study.<sup>(191)</sup> Electron beam curing of thin films of unsaturated polyesters is useful in the coatings industry. Copolymerizations of unsaturated polyesters with a variety of monomers, using electron-beam initiation, has been studied and compared.<sup>(178,179)</sup> Ultraviolet light will gel unsaturated polyester–vinyl monomer mixtures; however, the polymerization rate is too slow for commercial use unless photosensitizers, such as benzil, benzoin methyl ether, and diphenyl sulfide, are used. The UV light cleaves the photosensitizer to give free radicals for initiating copolymerization. Films and laminates may be cured readily with UV light, with curing accelerated by the absence of oxygen. Scientists at Hughes Aircraft have investigated this chemistry in the United States space program for fabrication of deployed space components cured by sunlight.

#### 12.2.7. Modified Unsaturated Polyesters

By using intermediates that contain nitrogen, silicone, and other different type atoms, it has been possible to prepare a variety of unsaturated polyesters, containing amide, amino, urethane, siloxane, and other heteroatom residues. Unsaturated polyesters containing amide moieties can be prepared by several techniques.<sup>(192–201,993)</sup> MA and fumaric acid have also been utilized for preparing a large number of unsaturated polyamides (see Sec. 12.11).<sup>(202)</sup> In one case,<sup>(194)</sup> ethylene glycol, MA, phthalic anhydride, and various diamines were condensed to give poly(ester-amides). The resins exhibited limited solubility in styrene. Cured methyl methacrylate blends of the copolymer exhibited physical–mechanical properties akin to cured conventional polyester–methyl methacrylate blends. Chlorendic, phthalic, and isophthalic acid–aziridine salts have been condensed with MA and glycols to prepare resins with both amide and ester links.<sup>(203)</sup> Laminates prepared from styrene blends of the latter resin exhibited properties comparable to typical cured polyesters.<sup>(203)</sup> Patents in this area, for the most part, claim these amide containing resins are useful in heat-resistant coatings for electrical insulation, adhesives for glass, and other coating applications.<sup>(197,204–211)</sup> Compression molding with smooth surfaces and low shrink have also been prepared from polyesters with amide residues.<sup>(212,213)</sup> Also, unsaturated poly(ester-amides) have been crosslinked with acrylates and methacrylates, using UV light or an electron beam, to obtain possible printing plates, cation exchangers, and textile coatings.<sup>(214–216)</sup> Production of polyesters in the presence of hydrazine or hydrazides of compounds such as oxalic or sebacic acid gives resins that are crosslinkable without



peroxides.<sup>(217)</sup> Hydrazine modification speeds up the polyesterification reaction and the nitrogen containing residues act as accelerators for decomposition of the peroxide initiators during curing.<sup>(218)</sup>

Unsaturated polyesters have been prepared from 1,3,5-tris[2-hydroxy-3-(allyloxy)propyl]isocyanurate, MA, glycols, and acids.<sup>(219–222,373,374)</sup> Even a low content of the isocyanurate ring has a favorable effect on the thermomechanical properties of cured laminates. This has been confirmed in other studies where glycidyl isocyanurates have been crosslinked with MA<sup>(223,224)</sup> and cured unsaturated polyester composites contained the melamine moiety.<sup>(450,1068,1128,1129)</sup>

Compounds such as *N,N*-diethanolaniline,<sup>(164,165,225,226)</sup> alkyl diethanol amines,<sup>(227–229)</sup> 2,2-bis(morpholino methyl)-1,3-propanediol,<sup>(230)</sup> and nicotinic and isonicotinic acids<sup>(231)</sup> have been used to prepare unsaturated polyesters with chemically bonded amino residues. Unsaturated polyesters with tertiary nitrogen residues may also be prepared by copolymerizing MA with glycols in the presence of amines such as aniline,<sup>(232)</sup> where aniline adds to the double bond. Diglycidyl maleate, when treated with glucoamine, gives a styrene-soluble amine containing polyester.<sup>(233)</sup> Styrene crosslinked morphilino substituted resins exhibit enhanced hardness and vicat softening at 158°F.<sup>(233)</sup> The glucoamine modified polyester, when crosslinked with styrene, was highly hydrophilic, as shown by the standard ASTM water absorption test. Amino resins speed up cure, due to enhanced initiator decomposition rates. The compound bis(2-carboxyethyl)aniline, when coreacted with MA, glycols, and other dibasic acids was found potentially useful for preparing electron-beam curable wood coatings.<sup>(234)</sup>

Unsaturated polyesters with urethane residues have received significant attention.<sup>(235–249,1001,1005,1006,1028,1031,1032,1048–1057,1069–1080,1135)</sup> In much of this work, diisocyanates have been used as a chain extender or intermediate to prepare urethane containing vinyl ester crosslinkers. For example, the toluene diisocyanate (TDI) adduct of 2-hydroxyethyl methacrylate combined and cured with a typical unsaturated polyester resin gave reinforced laminates with improved cracking resistance, rigidity, and translucent properties.<sup>(241)</sup>

Crosslinking polyurethanes in the presence of unsaturated polyester-styrene mixtures produce unique topologically interpenetrating networks.<sup>(242,1002)</sup> The cured mixtures exhibited one glass transition temperature ( $T_g$ ), intermediate in temperature to the  $T_g$  values of the component network. Modification of unsaturated polyesters with TDI is also useful for preparing thixotropic formulations.<sup>(240)</sup> The urethane residue contributes high adhesion and wear and corrosion resistance to cured polyesters. The use of MA-based polyester polyols, as intermediates in polyurethane foams and coatings, is discussed in Sec. 12.5.

Modifications of polyesters with maleimides have been explored by various techniques.<sup>(76,250–260,1029,1044–1046,1081)</sup> In many cases, the maleimide



or bismaleimide has received attention as a crosslinker, with polymerization initiated by peroxides, UV light, electron beam, and  $\gamma$  radiation.<sup>(261)</sup> Maleimides act as accelerators or sensitizers for  $\gamma$ -radiation ( $^{60}\text{Co}$ ) polymerization of unsaturated polyester–vinyl monomer blends.<sup>(1099)</sup> Using hydroxyalkyl substituted imides<sup>(250)</sup> and imides made from trimellitic acid,<sup>(262,1033)</sup> polyesters with terminal imide groups and macromolecular chains with both imide and imide–amide residues along the chain have been prepared and evaluated. In all cases, it is shown that the imide structure improves the thermal stability and corrosion resistance of the resins.<sup>(263–268)</sup>

The reactions of unsaturated polyester resins with benzonitrile oxide and  $\alpha$ -*N*-diphenylnitrone have been explored as a path to unsaturated polyesters with isooxazoline and isooxazolidine residues.<sup>(1030)</sup> Introduction of nitrogen-containing heterocycles into the resins increases the heat resistance of the cured products.

Silicone-modified unsaturated polyesters have received a fair amount of study.<sup>(269–278)</sup> The most interesting effort<sup>(279)</sup> consisted of reacting dimethyldichlorosilane with hydroxy-terminated polyesters to prepare block copolycondensates containing both unsaturated polyester and polysiloxane blocks. An example would be poly(ethylene adipate–co–maleate–b–siloxane). Such polymers, crosslinkable by UV, thermal, and/or chemical curing, exhibited improved heat-resistance properties. The siloxane residues appear to improve the heat stability of the resins, as well as promote adhesion to glass, steel, and plastics. The latter would be expected, since silane coupling agents vastly improve fiber–polyester bond strength.<sup>(280,281)</sup>

Carbonate-modified unsaturated polyesters have received some attention.<sup>(282–284)</sup> Where hydroxy-substituted bisarylcarbonates were used as intermediates,<sup>(283)</sup> polyesters with improved properties were claimed. Combinations of polycarbonates and unsaturated polyesters have recently been patented as ophthalmic lens materials.<sup>(1059)</sup>

Unsaturated oligoesters based on novolak-type phenol–formaldehyde<sup>(285–287)</sup> and toluene–formaldehyde or xylene–formaldehyde<sup>(288)</sup> resins exhibit attractive physical properties. The propoxylated novolak resins gave laminates and castings of high hardness, high flex, high impact, and excellent compression properties. It was pointed out earlier that novolak resins with isopropenyl residues have been crosslinked with MA, using free-radical initiators, to obtain unique thermosets.<sup>(78)</sup>

Polyesters with acetal linkages have been prepared from 2-vinyl-1,3-dioxane-5-methyl-5-carbinol,<sup>(289,290)</sup> 4-chloromethyl-1,3-dioxolane,<sup>(291)</sup> and other ester forming acetals<sup>(1042)</sup> to give unique casting resins. Tetrahydrofurfuryl alcohol, tetrahydrofurfuryl acrylate, and tetrahydrofurfuryl methacrylate have been used to prepare modified polyesters.<sup>(292)</sup> The cured systems exhibited air-curing properties and chemical-resistance characteristics. It has also been shown that MA and ethylene glycol will undergo a polycondensation

reaction with unsaturated aldehyde resin to give film-forming compositions.<sup>(293)</sup>

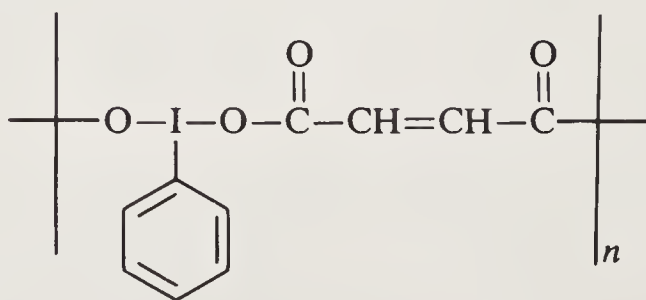
The glycol 2-butyne-1,4-diol and acetylene dicarboxylic acid have been reacted with MA and various glycols to prepare polyesters containing the acetylenic bond.<sup>(294)</sup> The soluble copolymers could be readily crosslinked.

The cyclopentadiene adduct of MA, i.e., *cis*-3,6-*endo*-methylene- $\Delta$ -4-tetrahydrophthalic anhydride (see Chapter 4) has also been used to prepare unsaturated polyester resins.<sup>(295,296)</sup> Similar to typical unsaturated polyesters, these resins may be combined with styrene and crosslinked. We note also that dicyclopentadiene can play the part of a glycol in polyester synthesis, giving a cost reduction for polyester production.<sup>(297-299)</sup>

Several groups have looked at organometallic-modified polyesters.<sup>(300-305,1061)</sup> Ferrocene containing polyesters exhibit high reactivity, good capacity for hot and cold curing, and properties suggesting utility in electrical insulation.<sup>(300,301)</sup> Poly(di-*n*-butyltin fumarate) exhibits water-repelling characteristics.<sup>(55)</sup> Organometallic chelates of Al, Co, Fe, Mn, Pb, and Ti perform well as accelerators or hardners for polyesters.<sup>(302,303,305)</sup> It is of interest to note that aluminium alcholates react with MA to give resinous materials.<sup>(306,307)</sup> Allyl-substituted antimony compounds with halogen residues provide fire-retardant properties.<sup>(308)</sup>

Polyesters prepared from bis(2-hydroxyethyl) sulfide have been explored as a method to obtain unsaturated resins with sulfide and sulfonium residues.<sup>(309)</sup> These materials are potentially useful for preparing hydrophilic coatings. Sulfur containing polyester resins have also been prepared from sulfur containing petroleum fractions with carboxyl groups<sup>(310)</sup> and by copolymerization of MA-1,2-alkylene oxide mixtures in the presence of sulfites or bisulfites.<sup>(1127)</sup> The sulfonic acid group containing polyesters are claimed to be useful as dispersants, liquefiers, leveling agents, sequestering agents, detergent additives, and boiler scale removal agents.

Organic polymers containing higher-valent iodine should exhibit interesting physical and chemical properties. This has been partially demonstrated by preparing a polyester of the structure shown, using MA and iodosobenzene starting materials.<sup>(311)</sup>



#### 12.2.8. Properties of Unsaturated Polyesters

The dynamic behavior of both cured and uncured polyesters,<sup>(312-314)</sup> as well as relating the molecular structures to the bulk properties or chemical



structures to the physical properties<sup>(102,315)</sup> have been extensively studied.<sup>(316–318)</sup> The crosslinking density versus viscoelastic properties<sup>(319)</sup> have been studied and related to various models.<sup>(320)</sup> Many studies have also centered on understanding the effects of the reactive diluent type and content on the physical properties of the cured resins.<sup>(321–322)</sup> It is well known that the choice of the reactive diluent monomer for curing of unsaturated polyesters for reinforced plastics is one of the principle factors in determining the properties of the end product.<sup>(60,61)</sup>

Unsaturated polyester resins can be formulated to be hard and brittle, tough and resilient, or soft and flexible. By the appropriate choice of intermediates, particularly to form the linear unsaturated resin, special properties can be built into the resin system.<sup>(318)</sup> As pointed out earlier (Table 12.2), the starting materials used with MA in polyesterifications have different effects upon the extent of isomerization of maleate to fumarate, and this in turn has a strong influence upon the final properties of the cured materials.<sup>(7)</sup> As shown in Table 12.2, the percentage of fumarate increases considerably as more sterically hindered glycols or aromatic acids are used in the formulations.<sup>(57)</sup>

Parker<sup>(7)</sup> studied the properties of cured polyesters versus level of unsaturation for systems composed of propylene glycol, diethylene glycol, and 1,3-butanediol in glycol maleate phthalate resins. At high levels of unsaturation the diethylene glycol series has higher flexural strength while 1,3-butanediol is better than the other two glycols at low levels of unsaturation. The flexural modulus of diethylene glycol drops off below the 50 mol % acid while the propylene glycol remains stiff. The flexural strength, flexural modulus, and tensile strengths of several saturated acids follow the order isophthalic > phthalic > diglycolic > adipic. Isophthalic acid is very useful for preparing resins with high flexural strength.<sup>(323–327)</sup> For example, at levels of styrene higher than 20%, plastics from isophthalic polyesters have significantly higher flexural strength than those prepared from phthalic anhydride. Isophthalic polyesters also have improved impact resistance, higher heat distortion, and superior adhesion to glass fiber reinforcement than phthalic anhydride resins. Rapp<sup>(443)</sup> recently describes a good procedure for preparing and processing isophthalate modified polyesters.

The creep,<sup>(328)</sup> stress intensity factors,<sup>(329,330)</sup> tensile,<sup>(328)</sup> elasticity,<sup>(328)</sup> and dynamic mechanical relaxation<sup>(331)</sup> properties of cured unsaturated polyesters have received considerable study. The tensile strength (TS) and tensile elongation (TE) at 25–120°C of a styrene crosslinked propylene glycol maleate phthalate polyester follows the following relationship:<sup>(332)</sup>

$$TS = 1.40F \times 10^{K/E}$$

where  $F$  is the number of styrene moles per crosslink,  $E$  the number of C and O atoms per crosslink, and  $K$  the constant that varies with temperature.

$$TE = E + 2F$$



From studying the unsaturated polyesters of polyalkylene glycol maleate adipates,<sup>(333,334)</sup> it was found that the tensile strength at break ( $\gamma$ ) of several polyesters was related to the concentration of double bonds in the copolymer ( $x$ ), the conversion of the crosslinking monomer styrene ( $A$ ), and its initial concentration ( $C_0$ ) by the following empirical equation.

$$\gamma = 988x + 4.1 \log (C_0 A) - 5.38$$

The compression, impact, and fracture properties of many cured unsaturated polyester resin formulations have been studied and reviewed.<sup>(318,335-337,1023)</sup> The compressive strengths of the rigid cured polyesters are of the order 15,000–30,000 psi. Cyclic glycols and specialty fumarate resins tend to raise this value, while aliphatic saturated acids lower the compressive strength. For aliphatic acids, the impact strength is proportional to the acid chain length.<sup>(318)</sup>

The shrinkage of cured unsaturated polyester compositions is mainly tied to the type of monomer used as crosslinker (Table 12.3).<sup>(318,338,339)</sup> A typical unsaturated polyester shrinks about 3%. In contrast, a general purpose polyester has a volume shrinkage of about 9%, with the difference attributed to the added monomer. One of the best monomers to reduce shrinkage, with a corresponding reduction of volatility and retention of reactivity, is *p*-tert-butylstyrene (TBS).<sup>(72)</sup>

The influence of end and center structures on polyester properties have received some study.<sup>(340-342)</sup> It appears that fumarate unsaturation near the chain ends in the isophthalate polyesters results in styrene-crosslinked resins with improved water resistance, heat distortion, and better color.

The resistance of cured unsaturated polyesters to chemical attack, i.e., corrosion resistance, has been the subject of many studies<sup>(343-356,1026)</sup> and the subject of several reviews.<sup>(352,357,1019)</sup> In general, polyester resins containing cyclic hydroxy compounds, such as hydrogenated bisphenol-A and 1,3- or 1,4-cyclohexanediol or 1,4-cyclohexanedimethanol, have improved chemical resistance.<sup>(358)</sup> Chemical resistance may also be obtained by employing neopentyl glycol,<sup>(359)</sup> isophthalic acid trimethyl pentanediol, and propoxylated bisphenol-A.<sup>(360-362)</sup> Isophthalic and terephthalic acids are much preferred over phthalic anhydride.<sup>(363)</sup> Diallyl phthalate imparts much better solvent resistance than styrene, but requires higher curing temperatures. The bisphenol resins appear to have the best overall alkali resistance.<sup>(346,351)</sup>

The weathering resistance and the effect of light stabilizers on cured unsaturated polyesters has been the subject of a number of studies.<sup>(364-369)</sup> As shown in Table 12.3, methyl methacrylate provides improved weathering resistance.

The heat stability of cured polyesters is strongly dependent upon the degree of crosslinking and the nature of the crosslinking monomer,<sup>(319,370-374,1022)</sup> as well as the structural intermediates.<sup>(318)</sup> In spite

of large differences in heat resistance of individual polyester formulations only small differences in the limiting temperature (149–168°C) can be detected. Tracking and bending resistance decrease with aging and weight loss can occur at temperatures  $>200^{\circ}\text{C}$ . Of the many allyl monomers studied, triallyl cyanurate appears to be particularly useful for preparing heat-resistant polyester resin products.<sup>(370–372)</sup>

The properties of unsaturated polyesters are also modified by a host of additives, such as thixotropic agents, chemical thickeners, fillers or extenders, fire-retardant chemicals, glass-fiber, and other reinforcement. A discussion of these areas is beyond the scope of this book. Most of this technology is disclosed in the extensive polyester patent literature. However, many books and review articles on polyester,<sup>(794)</sup> as well as manufacturers product literature, give good coverage of the subject.

### 12.2.9. Applications of Unsaturated Polyesters

Using the building blocks shown in Table 12.1, resin producers may prepare unsaturated polyester formulations to meet a broad spectrum of critical end-use requirements.<sup>(375)</sup> The estimated 1979 consumption of unsaturated polyester resins in the United States by end-use areas (percentage by weight) is shown in Fig. 12-1. The fortunes of unsaturated polyesters production and consumption closely follow the gross national product of the United States, with a correlation coefficient  $>90\%$  all through the 1970s. The present United States capacity for MA production is about 1.9 billion lb.

Reinforced thermosetting plastics are highly useful materials that offer a wide range of properties, depending on the selection of resin, reinforcement, and process. While there are several types of thermosetting resins from which to choose, and a large variety of possible reinforcements, the majority of applications utilize unsaturated polyesters, and glass fiber accounts for about 90% of reinforcement. Glass fibers are available in several forms, continuous strand, chopped fibers, mat, and woven structure. Extensive structure–property studies of glass-fiber reinforced polyesters have been accomplished,<sup>(47,376–382)</sup> with results showing plastics can be prepared that have flexural strength that rival aluminum. As shown in Fig. 12-1, about 80% of the unsaturated polyester production in the United States is fabricated into fiber-reinforced materials. For the future, the growth pattern for this combination continues to look very bright. Over the next five years the compound growth pattern is projected to be about 10–20%, keeping the industry growth profile well above the overall economy.

Marine applications are estimated to be the largest end-use category for polyesters, with the major use being in pleasure boats.<sup>(383–385,1018)</sup> This market has been experiencing percentage slippage due to the pleasure boat market



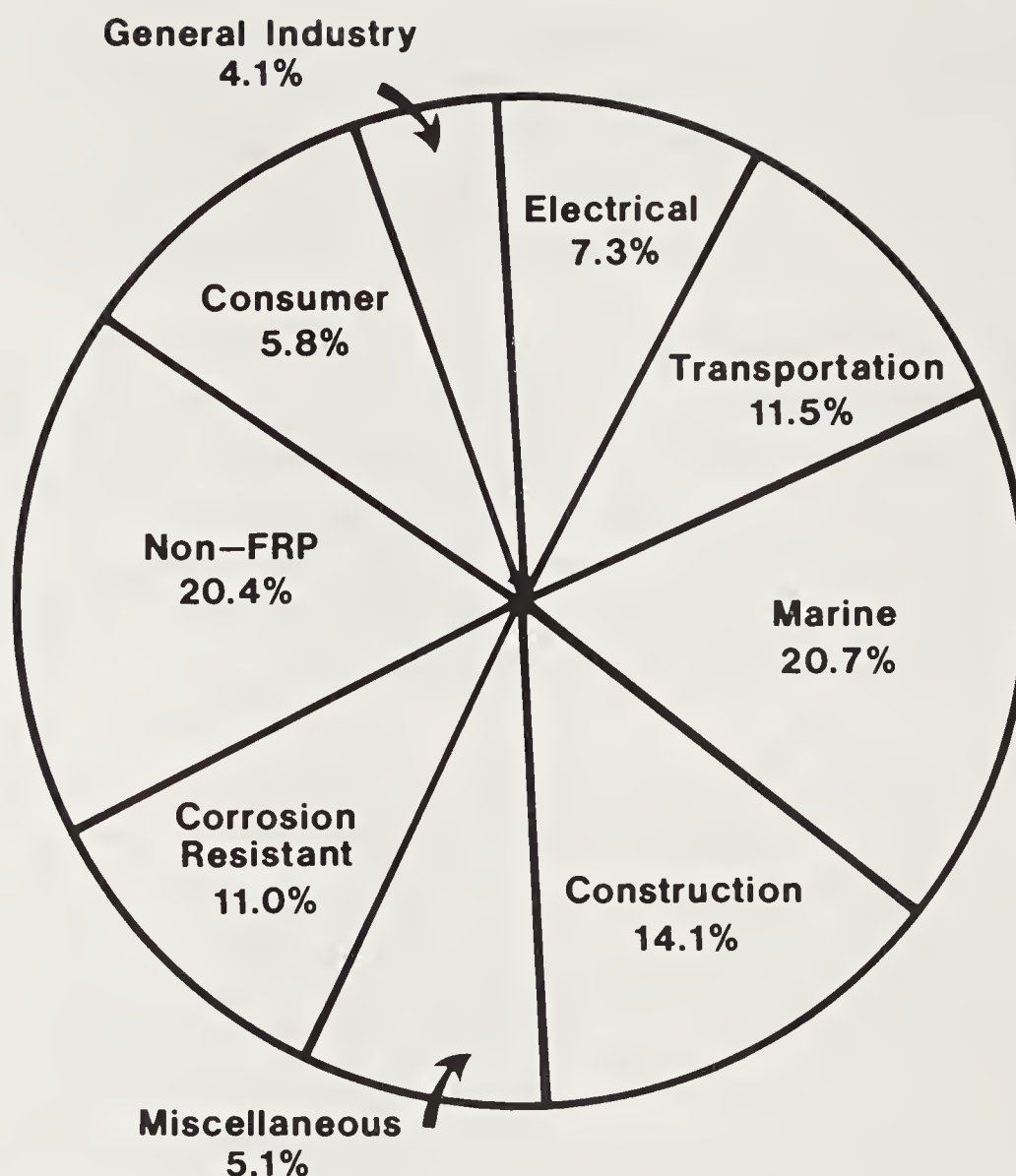


Fig. 12-1. End-use estimates for 1979 polyester resin market of 589 000 metric tons.

saturation and energy constraints. However, adoption of reinforced polyester technology for large commercial crafts could produce a substantial and stable market demand for the resins. In many cases fire-retardant resins are used for boat applications, satisfying government regulations. Polyester foams may grab a big slice of the marine applications, especially since a “unique family of liquid azo compounds” have been developed to foam these materials.<sup>(383,384,386,387)</sup> The same basic layup or sprayup techniques used to make boats is also used to make custom automobile bodies, truck cabs, trailers, motor homes, housing modules, concrete forms, and playground equipment. Procedures are being developed to substantially reduce styrene emission, by formulation of suppressed and low styrene content polyesters.<sup>(445,1130–1132,1137)</sup> The procedure provides a cost efficiency bonus that helps satisfy tightening OSHA requirements.

In the construction industry the largest use of polyester resins is centered about flat and corrugated sheet, unitized tub-wall units, shower stalls, and sanitary ware.<sup>(388)</sup> The sheet materials (panels) are useful for room dividers, roofing and siding, awnings, skylights, fences, and other applications. The major share of the base resins used in these applications may have limited



fire retardancy. However, fire retardancy is achieved through the use of fillers such as alumina trihydrate. The cultural marble lavatories use has no problem with fire-retardancy, since these castings are both hard to ignite and do not sustain combustion due to the high filler content.<sup>(389,390)</sup> In both the marine and construction application areas, specialty polyester gel coat resins are needed and used extensively to achieve production control and obtain the desired surface properties for the fabricated products.<sup>(391,392)</sup>

Corrosion-resistant resins for construction are experiencing an annual growth rate greater than 18%, due to environmental rules and regulations. These resins are used in process equipment and pollution control apparatus, such as ducts, storage tanks, tubing, pipes, hoods, and related items for industrial applications.<sup>(357,393–395)</sup> In the corrosion-resistant equipment area consumption of resin is expected to grow at an annual rate of about 10% over the next five years. The chemical storage tanks and large diameter pipe are made by the filament winding technique. About 60% of this market is composed of relatively low-cost general purpose resins produced from propylene glycol, MA, and isophthalic acid. Premium quality resins contain bisphenol-A resins and vinyl esters. The lower-density resins prepared from 2,2,4-trimethyl-1,3-pentanediol glycol and isophthalic acid or terephthalic acid look very attractive for this application.

The transportation area is a highly complex market, comprised of automotive, truck, and mass transit needs. Future growth in this market is strongly dependent upon a variety of factors. The factors supporting growth include:

- Increased U.S. mass transit push
- Growth of plastics in automobile use
- Improved polyester molding formulations
- Improved parts cost performance profile versus metals
- A continued growing demand for automobile weight reduction

Current and future factors retarding growth could include the following:

- A possible long-term decrease in automobile production
- Reduction of car model changes and recreational vehicle production
- Increased use of competing materials, such as thermoplastics and aluminum
- Continual shortage and price escalation of benzene used to prepare both styrene and MA
- Reduction of current 100-ppm styrene exposure limit to 50-ppm by the Occupational Safety & Health Administration

Advances made in coating molded parts in the mold, development of high-gloss, high-strength materials for filament winding and pultrusion fabrication methods, availability of improved low-profile compositions,<sup>(150,396–401)</sup> improved sheet molding (SMC),<sup>(399,402–410)</sup> and bulk molding<sup>(399,407–409)</sup>

compositions (BMC) have allowed for the observed substantial growth in the transportation market and several other areas.<sup>(411,412)</sup>

The low shrinkage, one-component molding systems (SMC) have given the auto manufacturer formulations for producing integrated front end panels, head lamp housings, spoilers, rear wheel opening covers, and various other components. No doubt the emerging foamed polyester technology will accelerate the use of unsaturated polyesters in the construction, marine, and transportation area,<sup>(384)</sup> since foamed polyester adds strength with cost reduction. The development of BMC systems has allowed the automobile manufacturer to fabricate heater housings, air conditioning components, fender extensions, lamp housings, hood scoops, trim rails, and other parts. The use of SMC techniques is also being evaluated for production of automobile structural parts. It is reported that a combination of the SMC and BMC process, i.e., thick molding compositions (TMC), is being evaluated in Japan for a variety of applications. The TMC technology should enjoy substantial future growth in molded reinforced polyester applications.

The advancement in molding compositions and techniques has also allowed for a very good growth rate in using polyester moldings for electrical appliances, hand tools, and motor housings.<sup>(413-415)</sup> The use of free-flowing granular formulations for the production of compression, transfer, and injection molded thermosets is destined for good growth.<sup>(415)</sup> Absence of post-shrinkage, good compatibility as binders, ease of blending with various inorganic fillers, and other advantages, make such materials very attractive in the electrical industry. Both SMC and BMC techniques are employed in this technology area. Dry pelletized or granular thermoset polyesters are also starting to grow at a rapid pace due to attractive properties and processing advantages.<sup>(416)</sup> This could well turn into the fastest growing area for unsaturated polyesters in electrical, appliance, and automotive markets. Other products prepared include street-light housings, circuit breaker bases, fire boxes, fuse holders, cable carriers, and switch gear parts. The good growth in this area has been fostered by the availability of fire-retardant, highly moldable materials with excellent electrical and physical properties.

The general industrial, consumer, and miscellaneous areas include such items as business machine and power tool housings, machine guards, furniture (FRP type), appliance parts, golf clubs, skis, luggage, snack table tops, food trays, tote boxes, stackable chairs, and public transportation seating. Pultrusion techniques are used for making fishing rod stocks and profiles from which slotted benches and ladders can be fabricated.

The Japanese use non-FRP in a unique manner for the production of a "polyester concrete," which is a highly filled mixture of resin and aggregate.<sup>(417,418)</sup> Asphalt paving can be significantly improved by unsaturated polyester resins.<sup>(419)</sup> The cured materials are identified by improved mechanical properties and resistance to water, acids, alkalies, and solvents.



The use of polyester to modify concrete is projected to experience good future growth.<sup>(420,421,1062,1134)</sup> Industrial polymer–concrete flooring compositions, exhibiting high surface hardness, scratch resistance, and other qualities may also be prepared from polyesters.<sup>(1004)</sup>

A recent and highly interesting use of non-FRP is Ashland's water-extendible polyester (WEP<sup>®</sup>), an emulsion of water droplets in polyester resin.<sup>(422–426)</sup> After curing, the water remains as a nonreinforcing filler. The cost of the material is quite low, due to the incorporation of a large amount of water. WEP<sup>®</sup> materials have been evaluated in many applications, including the encapsulation of waste radioactive materials<sup>(1017)</sup> and production of laminates.<sup>(1025)</sup> However, the most suitable uses appear to be the plaque and statuary areas. Funke *et al.*<sup>(442)</sup> recently reported on a procedure for emulsion polymerization of unsaturated polyesters without substantial formation of coagulum. Unsaturated polyester emulsions have been recently patented as wood coatings<sup>(1040)</sup> and blends of unsaturated polyester–epoxy resins in emulsions have been explored for the production of composites.<sup>(1041)</sup>

The nonfiber reinforced unsaturated polyesters, i.e., non-FRP, are dominated in the United States by the synthetic marble, automotive patching (body putty), and casting resins markets.<sup>(416)</sup> In Europe, substantial amounts of resin are used for high-gloss wood finishes.<sup>(427–429)</sup> Furniture parts,<sup>(430)</sup> simulated wood door parts, pedestals, trim elements, bed splats, lamp bases, wall plaques, simulated slate table tops, buttons, sewer pipe seals, and consumer hobby kits are additional examples for this area of polyester use. Other uses for non-FRP casting resins include varnishes, television tube interliners, electrical/electronic encapsulations, bowling balls, and pistol grips. Little use has been made of polyesters as adhesives.<sup>(431,432)</sup> However, a practically water-white polyester is employed to bond a protective heavy glass shield over the color television tube face.

The versatility of unsaturated polyester resin compositions, properties, and fabrication techniques, the design flexibility that can be achieved, and the relatively easy and economical mass production capability and new developments may be further understood and demonstrated by several other good articles and texts.<sup>(8,433–439,1024)</sup> Extensive patent literature, which is beyond the scope of this book, is also an excellent source of information on this large subject.

### 12.3. ALKYD RESINS

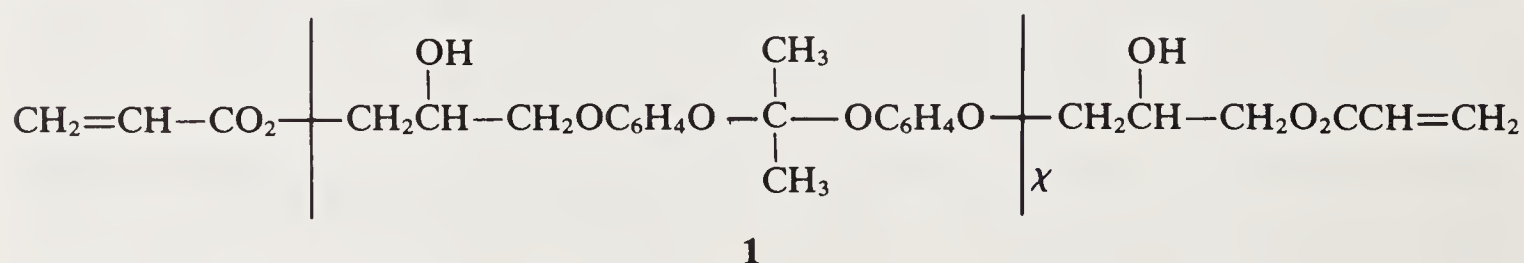
Alkyd resins are a special family of three-dimensional polyesters used by the coatings industry.<sup>(2–4)</sup> These materials are condensation products from dibasic acids or their anhydrides and trifunctional or tetrafunctional alcohols. Phthalic anhydride and glycerol are the most common raw materials. Fatty

acids are often used to modify and improve the alkyd resin to give air-drying properties.

Maleic anhydride can function both as a dibasic acid in the polyesterification reaction and a dienophile for Diels–Alder reaction with the fatty acid. The total functionality of the alkyd resin is significantly enhanced by MA. Thus, the replacement of phthalic anhydride by MA produces a more complex molecular structure with high viscosity and possible gelation. In normal alkyd production, MA or fumaric acid is usually restricted to about 1–10% of the phthalic anhydride content. Maleic anhydride incorporation improves color, processing time, and water resistance of the alkyd coating. Alkyd molding compositions are also being used to some extent in automotive and electrical applications.

#### 12.4. MALEATE–VINYL ESTERS

Vinyl ester resins or acrylic derivatives of epoxy resins are relatively new commercial resins, offering outstanding chemical or corrosion resistance. Two well known products marketed in this area are Dow's "Derakane" and Shell's "Epocryl" resins.<sup>(440)</sup> The vinyl esters are acrylate-terminated derivatives of diglycidyl ether resins, as shown with the derivative of bisphenol-A diglycidyl ether **1**.

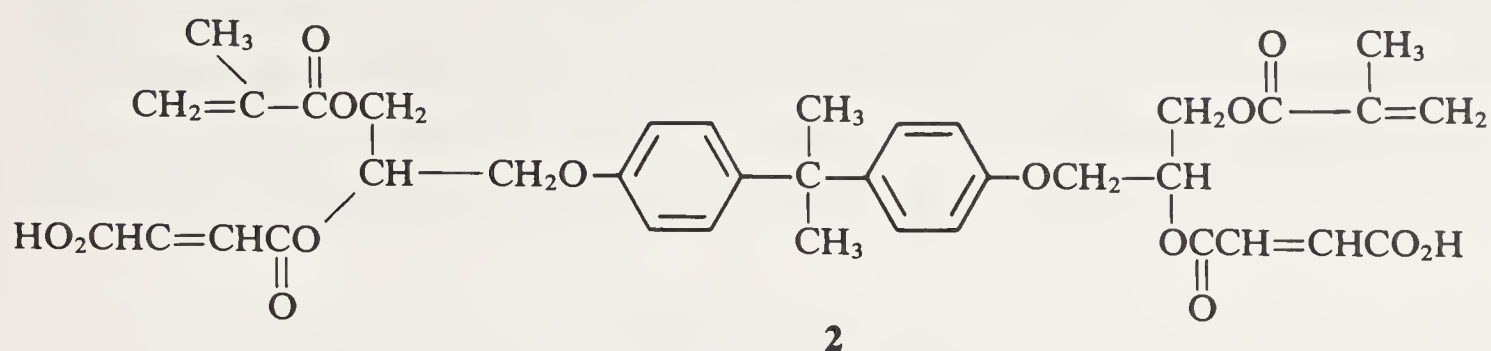


Unlike typical polyesters, vinyl esters have no internal ester linkage and, therefore, are less susceptible to hydrolysis. In addition, the great accessibility of the vinyl sites essentially ensures their complete consumption in polymerization reactions. Accelerators, stabilizers, and initiators have also received study for these systems.<sup>(447–449)</sup> Isophthalic acid and bisphenol-A based polyesters are in competition with the vinyl esters for the corrosion-resistance reinforced plastics market.

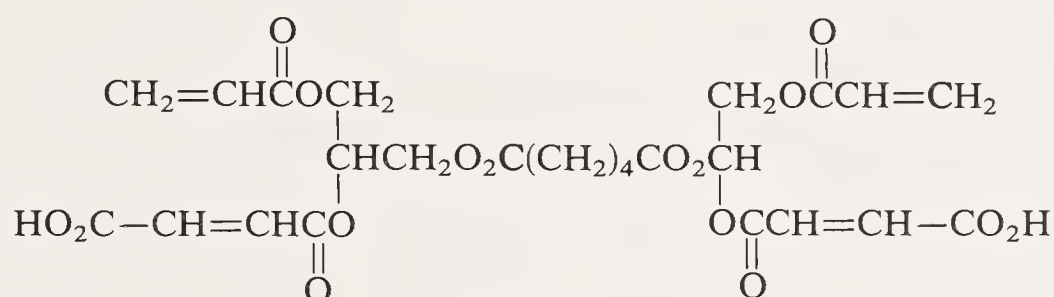
Analogous to the above, the diglycidyl ether of bisphenol-A and other epoxy resins have been condensed with MA,<sup>(74,451–458)</sup> to obtain electron-beam, UV-, and heat-curable coatings and laminating resins. Similar chemistry has been explored with the glycidyl esters and the epoxidized oils, where these materials have been reacted with MA to obtain coating resins.<sup>(459–463)</sup> In a typical example, the product derived from bisphenol-A diglycidyl ether and MA is blended with styrene and cured to obtain quality reinforced laminates, coatings, or electrical insulating materials. Tertiary amines are good catalysts for the epoxy resin–MA reaction.<sup>(464)</sup>



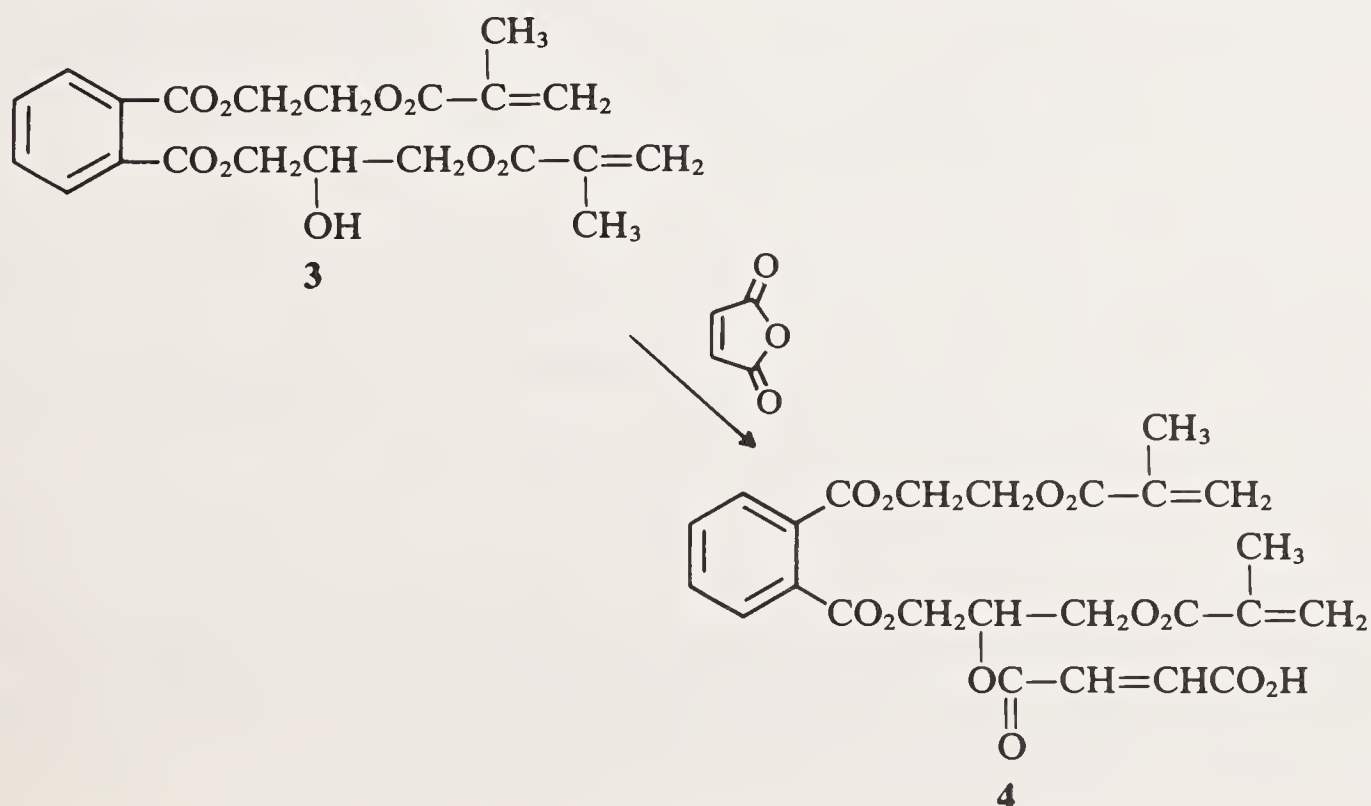
Bisphenol-A diglycidyl ether may also be treated with both acrylic acid or methacrylic acid and MA to prepare coating, laminating, and other resins with both vinyl ester and maleate residues.<sup>(465-475)</sup> The structure of a typical resin, using bisphenol-A diglycidyl ether, methacrylic acid, and MA, has the following structure **2**.



Glycidyl ethers of aliphatic alcohols<sup>(476)</sup> and glycidyl esters<sup>(477)</sup> have been exploited in an analogous manner to prepare coating and laminating resins. For example, diglycidyl adipate may be treated with acrylic acid and MA to give the following UV-curable coating.

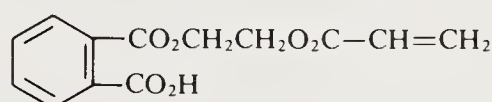
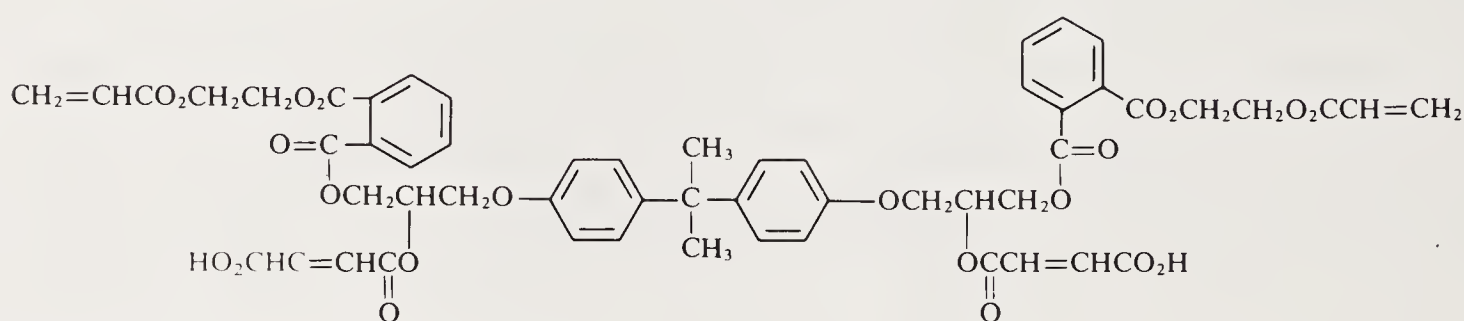


The concept for preparing vinyl esters with maleate residues has also been investigated by using hydroxyalkyl or glycidyl acrylate and methacrylate starting materials.<sup>(478-483)</sup> For example, phthalic anhydride was treated with hydroxyethyl methacrylate and the acid esterified with glycidyl methacrylate to prepare product **3**. Compound **3** was treated with MA to obtain a resin **4**

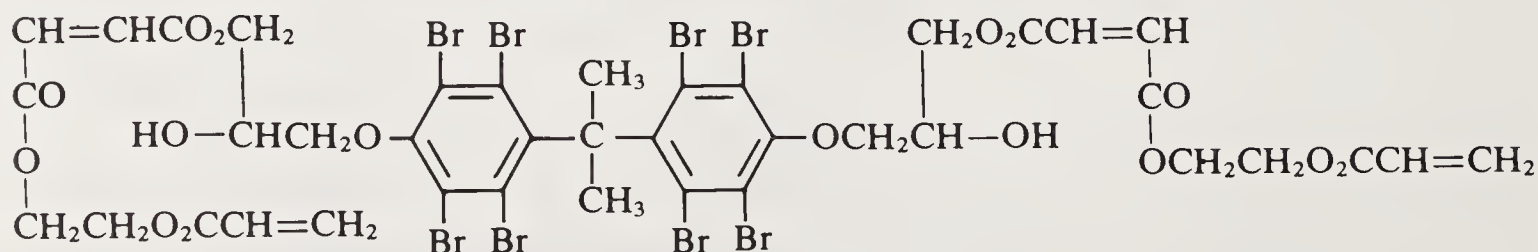


that could be modified with MgO or other metal salts to provide excellent molding materials.<sup>(480)</sup>

In another approach,<sup>(478,482-484)</sup> hydroxyethyl acrylate was treated with an equimolar amount of phthalic anhydride to obtain **5**. Compound **5** (2 moles) was treated with bisphenol-A diglycidyl ether, followed by esterification of the hydroxyl residues by MA to obtain **6**. Resin **6** when blended with vinyl monomers, such as styrene, and cured provides excellent flexible coatings, castings, and corrosion-resistant laminates. Modification of this concept has also been used by others to prepare radiation-hardenable coating formulations.<sup>(990)</sup>

**5****6**

Hydroxyethyl acrylate may be treated with MA and the reaction product subsequently treated with glycidyl ethers to prepare vinyl ester resins, with the maleate or fumarate residue within the resin chain.<sup>(485-488)</sup> This concept is demonstrated with the brominated derivative of bisphenol-A diglycidyl ether<sup>(488)</sup> starting material to prepare resin **7**. Materials of this nature may be blended with other monomers and cured to give high heat distortion, corrosion-resistant and flame-resistant plastics.

**7**

A great variety of other techniques are continuing to be explored for preparing and using resin systems containing both the reactive acrylate (methacrylate) and maleate or fumarate residues.<sup>(495-507,1016)</sup> The great



industrial interest in this area is nurtured by the knowledge that these unsaturated epoxy-ester resin systems have the good properties of epoxy resins, excellent crosslinking properties, and the processability of unsaturated polyesters. Mixtures of triethylene glycol dimethacrylate, MA, phthalic anhydride, and styrene, combined with peroxides and accelerators, may be readily cured to give useful coatings.<sup>(508)</sup> In this procedure, simultaneous condensation and addition reactions occur to give the cured product.

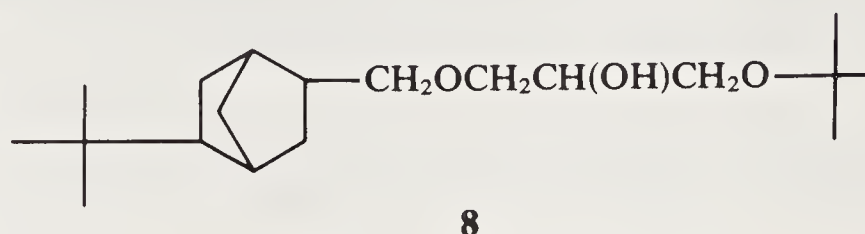
## 12.5. MA MODIFIED ADDITION POLYMERS

The concept of treating addition polymers or copolymers with pendent or terminal hydroxyl residues with MA has been extensively explored and disclosed in the patent literature. Using this technique, it is possible to prepare a special type unsaturated polyester with potential applications in films, sheets, and moldings.

Partially saponified ethylene-vinyl acetate and poly(vinyl acetate) copolymers<sup>(509-513)</sup> or poly(vinyl alcohol)<sup>(514-523,1012,1037,1038)</sup> may be treated with MA to obtain materials with pendent maleate or fumarate residues. It is also possible to transesterify a poly(ethylene-vinyl acetate) copolymer, using  $\text{HgCl}_2$  catalyst at  $100^\circ\text{C}$ .<sup>(511)</sup> Cotton materials have also been treated with MA to obtain fabric with monohydrogen maleate residues.<sup>(522)</sup> Materials of this nature have been combined with divinyl benzene, dimethacrylates, and other compounds and cured with peroxides to obtain molding resins. Ionomer-type materials result when partial neutralization of the carboxyl groups is achieved. The MA-modified poly(vinyl acetal) resins are potentially useful adhesives for window safety glass.<sup>(1012)</sup>

Polybutadiene has been modified in several ways with MA. In one case, poly(butadiene) with terminal hydroxyl groups have been treated with MA and epoxides to prepare polybutadiene-polyester block copolymer.<sup>(523,524)</sup> These materials, when blended with other monomers, initiators, etc., were used for preparing elastomers and molding materials with excellent tensile and flex strength. Others have also treated  $\alpha,\omega$ -polybutadiene glycols with MA, and crosslinked the materials with various vinyl monomers, using ionizing radiation as well as free-radical initiators.<sup>(525-528)</sup> Tough, flexible and attractive products, such as coatings, moldings, castings, and elastomers, may be produced. The MA condensation product of 1,2-poly(butadiene) and 1,4-poly(butadiene) have also been evaluated in electrophoretic coatings and adhesives applications.<sup>(529,530)</sup> Hydroxy-terminated polybutadienes, after grafting with styrene, chlorostyrene, and other materials, have also been esterified with MA.<sup>(531)</sup> When blended with monomers such as diallyl phthalate and initiators, the materials provided excellent laminating or molding resins. It is possible to carboxylate polybutadiene with acid catalysts.<sup>(532,533)</sup>

When combined with vinyl monomers, MgO, and catalysts, these materials also give attractive laminating resins. Hydrogenated polybutadienes with hydroxyl groups<sup>(534,535)</sup> and the copolymer **8** prepared from bicyclo[2.2.]hept-2-ene-5-yl-methyl 2,3-dihydroxy-propyl ether<sup>(536)</sup> have also been treated with MA to give high-strength electrical insulating materials.



A large variety of addition copolymers and terpolymers, prepared from hydroxyalkyl acrylates and/or methacrylates have been treated with MA to prepare polymers with pendent maleate residues.<sup>(491,537-545,1058)</sup> An addition polymer prepared from ethyl acrylate-hydroxypropyl methacrylate-styrene was treated sequentially with MA and propylene oxide.<sup>(538)</sup> Blends of these polymers with vinyl monomers were cured with peroxides to obtain films with physical properties better than regular cured unsaturated polyesters. In another example, a styrene-butyl acrylate-hydroxyethyl methacrylate terpolymer was treated with MA to obtain a molding resin.<sup>(541)</sup> When blended with styrene and cured with peroxides, the molding exhibited low shrink (less than 5%) and Rockwell hardness (M scale) 55. The same chemistry and technology have been explored for preparing radiation-curable coatings.<sup>(491)</sup>

Acrylic copolymers with pendent hydroxyl moieties have been converted to polymers with both pendent fumarate and acrylic ester residues.<sup>(546,547)</sup> In the concept, the acrylic copolymer with pendent hydroxyl groups is esterified with MA and the resultant carboxyl moiety subsequently also esterified with glycidyl methacrylate. These materials may be combined with vinyl monomers and cured by an electron beam or UV radiation to give attractive metal coatings.

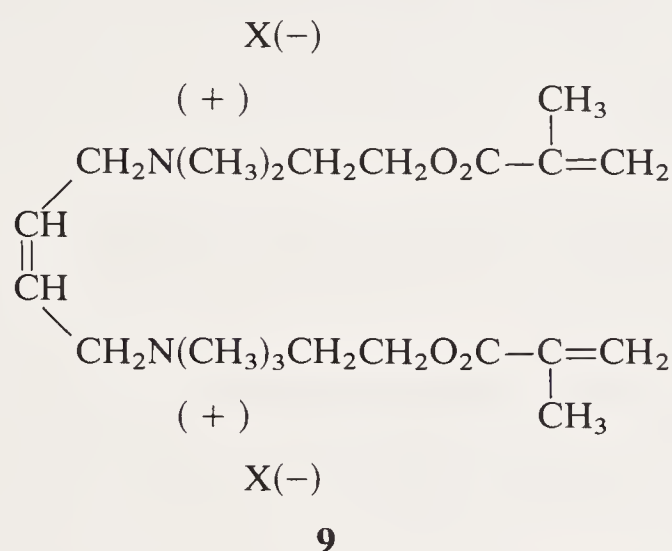
Allyl alcohol-styrene copolymers have been esterified with MA.<sup>(548,549,1010,1011)</sup> The resultant copolymers may be blended with styrene and cured with peroxides to obtain translucent, rigid laminates with good corrosion resistance.<sup>(548)</sup> The same copolymer has been cured with melamine derivatives, providing potentially useful coatings,<sup>(549)</sup> formulated to obtain aqueous air-drying primers,<sup>(1010)</sup> and modified to obtain anodic electrocoating paints.<sup>(1011)</sup> Films of terpolymers containing allyl alcohol and butadiene monomers, when crosslinked with MA, are possible coating materials.<sup>(497)</sup>

Epoxy-terminated poly(butadiene),<sup>(550,551)</sup> epoxidized polybutadienes,<sup>(552)</sup> and acrylic copolymers with pendent epoxide<sup>(553)</sup> moieties have also been treated with MA, to obtain free-radical curable materials. These materials looked attractive for preparing rubber compositions, laminating resins, coatings, and photoresists.



Several other acrylic copolymers with pendent maleate-cinnamoloxy,<sup>(554)</sup> maleate- $\beta$ -(2-furyl) acrylate,<sup>(555)</sup> and the maleate derivative of hydroxyalkyl arylamine<sup>(556)</sup> groups are shown to be potentially useful for photopolymerizable printing plates. Polyacrylonitrile fibers have been treated with MA to obtain modified fiber with improved strength, heat stability, and acid stretching ratio.<sup>(505)</sup>

It is interesting to note that *N,N*-dimethylaminoethyl methacrylate has been quaternized with 1,4-dihalobutene to prepare intermediate **9**. It is claimed that intermediates such as **9**, when combined with MA and photoinitiators, are highly useful for preparing photoconductive paper coatings.<sup>(557)</sup>



Mixtures of maleated poly(vinyl butyral) with alkyl acrylate and methacrylate monomers and photosensitizers may be irradiated from a high-pressure Hg lamp to give an excellent glass adhesive.<sup>(558)</sup> Glass plates bonded with the mixture show no change on heating for 100 h at 170°C.

## 12.6. ISOCYANATE CROSSLINKED POLYESTERS

A variety of hydroxy-terminated unsaturated polyesters have been evaluated as intermediates in polyurethane foams.<sup>(559-570,1034,1134)</sup> These intermediates include the ethoxylated or propoxylated derivatives of lignin-, sorbitol-pentaerythritol-MA condensation products.<sup>(559,567-571)</sup> MA has also been blended with poly(vinyl chloride) and diisocyanates to obtain cellular PVC materials.<sup>(572-574)</sup>

Hydroxy-terminated unsaturated polyesters have been modified, chain extended and crosslinked, with polyisocyanates to obtain structural plastics that exhibit good gloss, chemical resistance, flexural strength, deformation resistance, improved impact, and other attractive properties. Adhesion promoter resin for glass fiber-polyester laminates may also be prepared from chain-extending hydroxy-terminated polyester with diisocyanates and capping the free isocyanate groups with aminoalkylalkoxy silanes.<sup>(575)</sup> Unsaturated

polyesters with hydroxyl groups may be modified with isocyanates to provide a variety of coatings.<sup>(575-585)</sup> In most cases these have been oil-modified, moisture-cured systems. It has also been shown that MA may be used to modify hydroxy-terminated polyurethanes to provide possible emulsion coatings.<sup>(586,587)</sup> Other procedures have been evaluated and patented to prepare polyurethane coating intermediates containing the maleate residue.<sup>(588-590,1003)</sup>

Highly crosslinked cellular materials, having predominately cyclic imide structures in the main chain, may be prepared from a cyclic anhydride reaction with polyisocyanates.<sup>(535)</sup> For example, mixtures of MA, diisocyanates, surfactant, and water may be molded, with loss of CO<sub>2</sub>, into fine-celled structural materials.

## 12.7. POLYTHIOL CROSSLINKED POLYESTERS

The addition of thiols to olefins, giving molecules with thioether or monosulfide linkages, is well documented. In the presence of peroxides or UV light, the reaction gives anti-Markownikoff addition products. Using dithiols and diolefins, a wide variety of polythioethers have been prepared and evaluated.<sup>(591,592)</sup>

Polythiols have received a fair amount of attention as crosslinkers for unsaturated polyesters.<sup>(593-600)</sup> A great variety of polyester compositions and polythiol blends have been cured and evaluated as flexible casting resins, adhesives, carpet backing resins, paper and leather coatings, foams, textile coatings, sealants, printing inks, and can coatings. The chemistry is valuable for preparing 100% reactive, liquid systems that cure at room temperature and emit no volatiles. With expanding environmental constraints and need to cure materials with low energy demand, this chemistry could be very useful to satisfy future demands for various coatings, adhesives, and sealants.

Selective free-radical polyaddition of dithiols to the allylic double bonds of diallyl maleate results in the synthesis of unique sulfur containing polyester with maleic unsaturation.<sup>(601)</sup> In the presence of base, Michael-type addition of the thiol group with the maleate double bond occurs. The unsaturated polyester may be crosslinked both by vinyl monomers, such as styrene, with peroxides or with polythiols in the presence of base.

MA may be condensed with compounds such as 2-mercaptoethanol to give resinous materials.<sup>(602,603)</sup> The carboxyl residues of these resins may be esterified to give oil additive polymers or the carboxyl polymer used in ion exchange, pigment adjuvant, and other applications.<sup>(602,603)</sup> Rubbery sulfur foams prepared from polysulfide reaction with MA may have several unexplored uses.<sup>(1036)</sup>



## 12.8. MISCELLANEOUS POLYESTER CONDENSATIONS

As mentioned in the uses section (Sec. 12.2.9), a substantial amount of unsaturated polyester resin is used in Europe as high-gloss wood coatings. This market has never developed to any great extent in the United States. This is not to say that substantial effort has not been devoted to this cause, as shown by the patent literature.<sup>(604–608)</sup> Interest in the unsaturated polyester resin coatings in the United States has mainly centered about radiation-curable systems. The lack of acceptance comes about because the polymerization (crosslinking) of unsaturated polyester resins is strongly inhibited by atmospheric oxygen, with the result that the surface of such coatings remains soft and tacky. Addition of wax to the formulation helps prevent air inhibition of surface cure. Formulations have also been developed that contain allyl residues, which speed up surface cure. However, this step has unattractive economics and other problems.

The crosslinking of hydroxy-terminated unsaturated polyesters, with melamine derivatives<sup>(609–619)</sup> and urea-formaldehyde condensates,<sup>(620–622)</sup> has been explored for preparing coatings, adhesives, and other end-uses. Crosslinking of unsaturated polyester resins modified with hydroxyalkyl-substituted amines with melamine-formaldehyde condensates is useful for generating pressure-sensitive adhesives. The Diels–Alder reaction may also be used to crosslink polyesters.<sup>(623)</sup> For example, heating blends of ethylene glycol disorbate with unsaturated polyester gives crosslinked films. Fulvenes<sup>(624)</sup> and 2-vinylbutadiene<sup>(625)</sup> have also been used to crosslink polyesters by the Diels–Alder reaction (see Chapter 4).

Effort has been devoted to preparing water-based enamels from modified unsaturated polyester resins.<sup>(623–635)</sup> In some cases, the hexakis (methoxymethyl) melamine-cured materials looked good in electrodeposition coatings.<sup>(636,637)</sup> This has generally not been a productive procedure when compared to the maleinized oil–polyester route.<sup>(638,639)</sup>

## 12.9. CURING OF EPOXY RESINS

Epoxy resins require a curing agent or crosslinker in order to convert them to thermoset materials. In the curing process, both the epoxide moiety and the hydroxyl groups may be involved, and the curing takes place at ambient or elevated temperatures. Over the years, a great variety of chemical reagents have been evaluated as hardeners for epoxy resins. The curing agents most commonly used are amines, Lewis acids, cyclic anhydrides, and various phenolic, urea, or melamine type resins.

MA<sup>(640–659)</sup> and derivatives of MA<sup>(660–671,992,994,1020,1021,1060,1067)</sup> have had considerable attention as crosslinkers for many different types of epoxy resins,

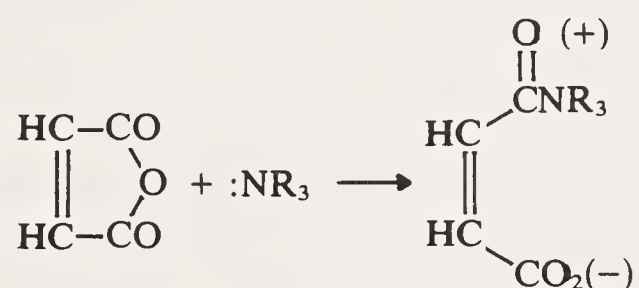




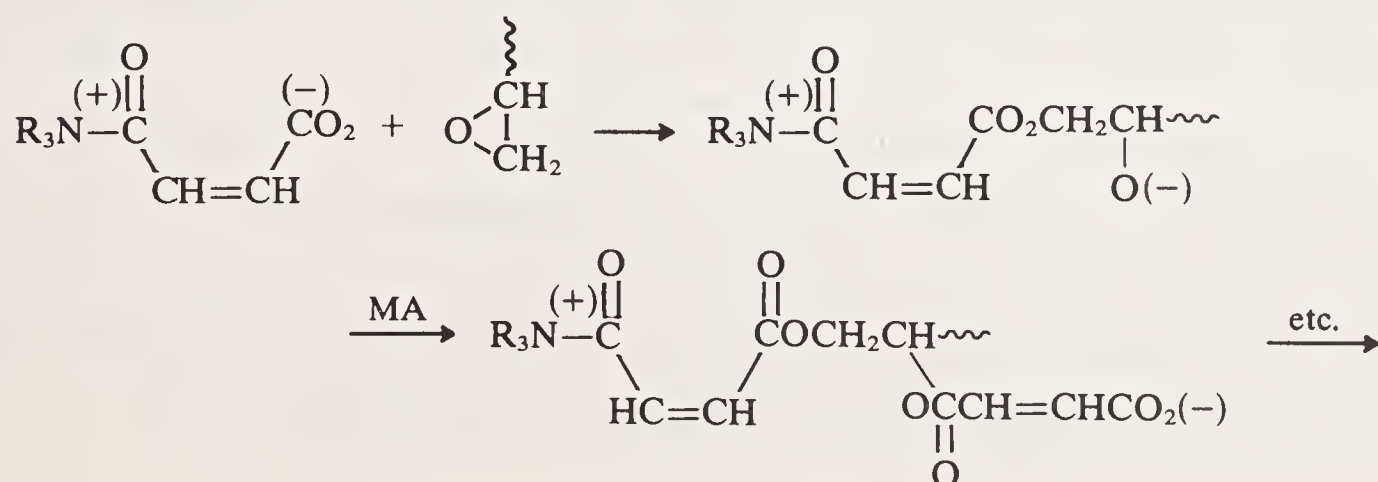
The above mechanism is highly simplified, since etherification may occur in some systems. However, it can generally be concluded that the anhydride-hydroxyl reaction dominates the epoxy-hydroxyl reaction, allowing very little etherification to occur. If only one active hydrogen (hydroxyl group) were present at the start, it would be expected that the optimum properties for the system would be found at an anhydride/epoxy ratio of 1:1, with no etherification.

Evidence has been published<sup>(708)</sup> suggesting that the reaction may involve a termolecular transition state. There is also evidence that etherification tends to not occur until the gel point is reached.<sup>(709)</sup> It can only be concluded that the curing reaction is generally quite complex. Especially, when consideration is given to the fact that depending on the nature of the formed carboxyls, some anhydrides will be more reactive with the epoxy group and others will more readily promote etherification. The activity and/or optimum hardening time and the degree of conversion will be governed to some extent by the reaction temperature, content of hydroxyl residues, and the anhydride content.<sup>(679,690)</sup> Thus, no simple expression is available for the determination of the optimum anhydride/epoxide (A/E) ratios for all anhydride curing agents. It has been generally concluded that for optimum performance with an uncatalyzed A/E system, the hydroxyl content should be controlled, the cure temperature should be reasonably high and long, and the A/E ratio should be adjusted to the specific curing conditions.<sup>(679)</sup>

Where Lewis bases, such as tertiary amines, are employed with the anhydride, the base reacts preferentially with the anhydride to generate a carboxyl ion:



The carboxyl anion reacts with an epoxy residue, generating a new anion, which may then open a second anhydride ring, to give the crosslinked structure:



The reaction rate has been shown to be dependent on the accelerator concentration.<sup>(710-712)</sup> Reaction rate studies generally support the above simplified picture for the effect of accelerators.<sup>(678,689,708)</sup>

The structure and properties of epoxy resins cured with MA have been compared with a variety of other anhydrides.<sup>(691,694,696,697,699,704-706,713-722)</sup>

Also, the properties of MA-cured resin have been compared with amine-cured resins.<sup>(694,700,716,723-728)</sup>

Properties such as heat distortion, heat resistance,<sup>(729-731)</sup> light aging,<sup>(732,733)</sup> flexural strength, toughness, solvent resistance, dielectric strength, electrical,<sup>(734)</sup> ablation,<sup>(735)</sup> creep,<sup>(736)</sup> tracking resistance,<sup>(737)</sup> Rockwell hardness,<sup>(738)</sup> and other properties, and variations of properties with thermal aging have been evaluated. Lack of compatibility of MA with epoxy resins causes a nonuniform distribution of crosslinker and this brings about cross grain formation.<sup>(739)</sup> This and other considerations make it fortunate that mixtures of several anhydrides are liquids and some olefin-MA adducts are liquid hardening agents.<sup>(663)</sup> Anhydride-cured systems have better heat distortion and aging properties, when compared with amines. However, amine crosslinked systems will cure at ambient conditions. MA gives greater crosslinking than hardeners such as phthalic anhydride. Several reviews give a good discussion of the physical and chemical properties of anhydride-cured epoxy resins.<sup>(679,680,716)</sup>

It was pointed out earlier,<sup>(663-700)</sup> many MA derivatives or adducts<sup>(992)</sup> have been prepared and evaluated as hardeners for epoxy resins. In general, these have been adducts of animal or vegetable oils,<sup>(740-745)</sup> Diels-Alder (see Chapter 4) adducts,<sup>(746-757,992)</sup> and ene (see Chapter 5) derivatives of olefin polymers or copolymers.<sup>(758,759)</sup> Long-chain poly(alkylene oxide)<sup>(760-761)</sup> and hydroxy-terminated poly(butadiene)<sup>(762)</sup> have also been treated with MA to provide carboxylated epoxy resin hardeners. Reaction of MA with dicyclopentadiene and subsequent reaction of the maleate product with aliphatic diamines has been explored as a route to produce oligomeric amides for curing epoxy resins.<sup>(1039)</sup> We note also that some attention has been given to curing unsaturated polyesters with epoxy resins.<sup>(763,764,1043,1065)</sup> For the most part, this effort has been directed to providing improved and tailored crosslinkers for epoxy resins. From such efforts, industry now has a wide range of both liquid and solid acid anhydride agents for curing epoxy resins. The most acceptable materials appear to be the liquid anhydride agents<sup>(751,765-767)</sup> and mixtures.<sup>(768-775)</sup> The anhydride-cured epoxy resins appear to be most useful in electrical applications and filament winding where long working life, low viscosity, high heat stability, and good chemical resistance are very important attributes. Those interested in additional information on the MA-epoxide reaction for preparing thermosets for coatings, adhesives, laminates, moldings, potting compositions, sealants, composites, and other applications are advised to also consult the extensive patent literature on the subject.



## 12.10. MALEIMIDES AND POLYIMIDES

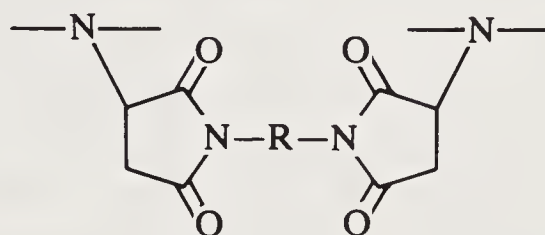
It was discussed earlier (see Chapter 3) how MA may be converted to maleimide and *N*-substituted maleimides, by using ammonia, urea, and primary amino compounds and a variety of synthetic techniques.<sup>(776–783)</sup> Maleimides and substituted maleimides readily undergo free-radical-induced homopolymerization<sup>(779–793,795–800,991)</sup> and copolymerization (see Chapter 8) with vinyl monomers.<sup>(776,801–813,889)</sup> In view of the fact that those polymers and copolymers are a potential source of heat- and chemical-resistant materials, it is only natural that other polymeric systems would be modified to contain maleimide residues. The use of maleimides and bismaleimides in condensation polymerization systems is briefly discussed in this section, since there is great activity now going on to exploit these MA derivatives.

It was mentioned in Sect. 12.2.7 that unsaturated polyesters have been modified with maleimides to obtain composites with improved heat resistance. Other polymeric systems, such as epoxy,<sup>(779,780,814–837,1085–1095,1112)</sup> polysiloxane,<sup>(838)</sup> cyanoacrylates,<sup>(849–842)</sup> urethane,<sup>(843,844)</sup> urethane-acrylate,<sup>(845,846)</sup> and saturated polyesters<sup>(1117)</sup> have also been modified with maleimides to obtain improved coatings, adhesives, laminates, and fibers. The vulcanization of polyolefins and diene polymers with maleimides<sup>(847–852)</sup> gives elastomers with improved heat resistance (see Chapter 11). Compounding poly(vinyl chloride) with maleimide gives crosslinked materials with good solvent and heat resistance (see Chapter 11).<sup>(853)</sup> In most cases, catalytic amounts of peroxides are needed to bring about crosslinking of the copolymers, including both unsaturated hydrocarbon polymers and polyethylene materials.<sup>(844)</sup> Combinations of maleimides and allyl substituted materials,<sup>(854–856,995,1085–1090)</sup> as well as polybutadienes (see Chapter 11) also cure readily with peroxides to give varnishes and casting and laminating resins useful in electrical applications. Photocrosslinkable single-phase systems containing bismaleimides and diallyl phthalate prepolymer are also useful for manufacturing components for electrical applications.<sup>(1086)</sup>

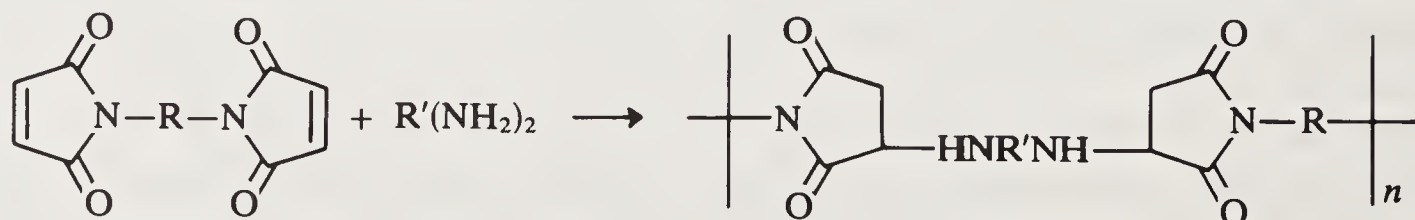
The condensation reaction between MA and aliphatic or aromatic polyamines has been used to prepare a large number of bismaleimides<sup>(830,839–841,846,848–850,857–869,1082,1123)</sup> and trismaleimides.<sup>(870–872)</sup> Polystyrene has been treated with *N*-chloromethyl-maleimide, using a mild Friedel-Crafts procedure, to prepare polymer with pendant maleimide residues.<sup>(873)</sup> Poly(vinyl alcohols)<sup>(1083)</sup> and alternating styrene-MA copolymer or polymers with pendent epoxide residues<sup>(1084)</sup> have been converted to polymers with pendent maleimide moieties. All these multifunctional maleimides may be polymerized thermally,<sup>(1118)</sup> with peroxides, UV light,<sup>(872–882,888,996)</sup> and  $\gamma$  rays<sup>(890)</sup> to obtain heat-resistant coatings or laminates. Polyethers with pendent maleimide residues have been crosslinked with

electromagnetic radiation for a variety of photomechanical applications.<sup>(996)</sup> Manecke and Middeke<sup>(1083)</sup> showed the maleimide groups containing macromolecular supports were useful for immobilization of enzymes, having controlled enzymatic activity. In several cases, water-dispersible and electrodeposition resins have been formulated from maleimides, to prepare attractive coatings.<sup>(883–886)</sup> Maleimide blends with bismaleimides<sup>(887)</sup> or polyfunctional maleimides alone may be converted with heat ( $>200^{\circ}\text{C}$ ) or peroxides to give potentially valuable heat-resistant films, coatings, adhesives, laminates, and molded articles,<sup>(859,863–867,869–885,891,1117–1120)</sup> exhibiting excellent tensile and flexural strengths.<sup>(892–897)</sup> The crosslinked aliphatic bismaleimides are stable up to ca.  $400^{\circ}\text{F}$ .<sup>(898)</sup> The flexural strength and modulus of maleimide laminates, in some cases, are superior to glass-reinforced epoxy and silicone composites.<sup>(899)</sup>

It has long been recognized that amino containing polymers, such as gelatin, polyethylenimine, and polymers bearing amino end-groups may be crosslinked by bismaleimides.<sup>(844,900)</sup> The crosslinking and chain-extending reactions involve a Michael-type condensation reaction between the active hydrogen–nitrogen residues and the double bond on the maleimides, with the results illustrated as follows:



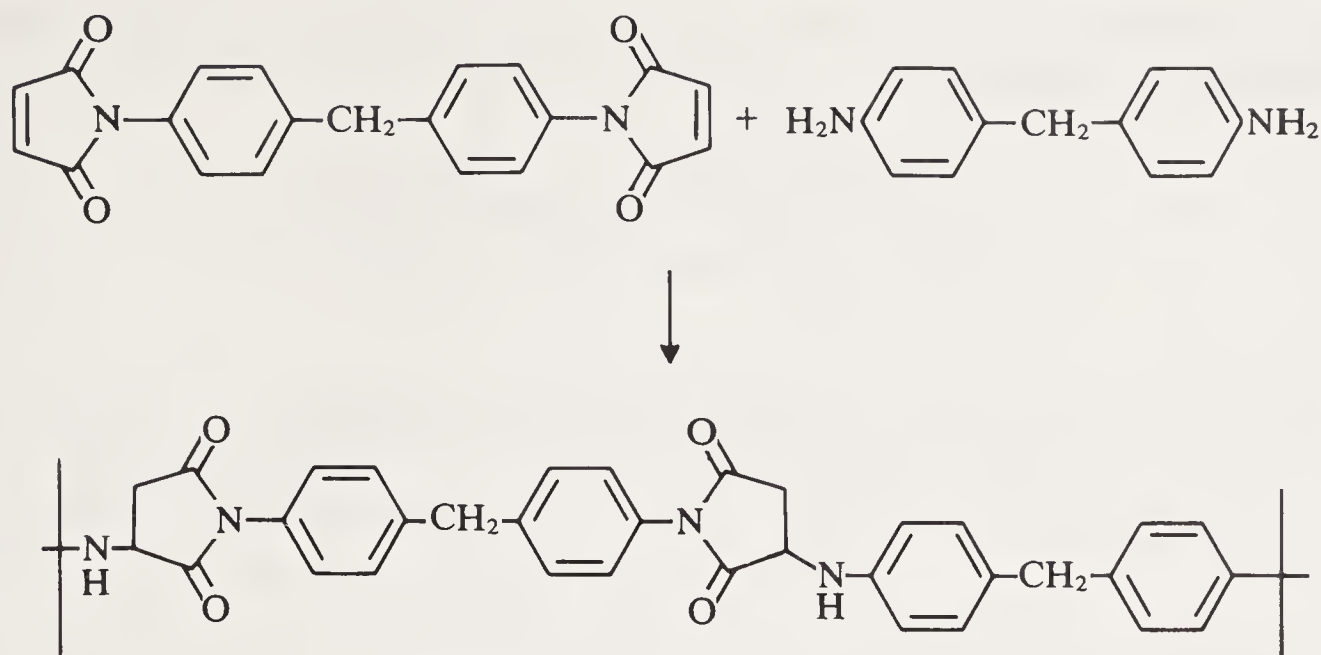
Using this reaction scheme, a novel approach to attaining low-temperature processing of maleimides, without the evolution of volatiles, has been achieved. Morpholine and imidazole (derivatives) as well as other tertiary amines, are catalysts for the condensation reaction.<sup>(997,1105)</sup> The concept, as shown below, consists of reacting bismaleimides with diamines to obtain poly(amino–bismaleimides).<sup>(901–918,1103–1109)</sup>



Rhodia, Inc. (Rhône-Poulenc S.A.) markets a copolymer prepared by this concept, Kinel, which is prepared from the reaction of *N,N'*-[4,4'-diphenyl(methane)] bismaleimide and 4,4'-diaminodiphenyl methane.

The physical and chemical properties of Kinel and Kelimide heat-resistant molding resins have been the subject of reviews.<sup>(919,920)</sup> Versions of this chemistry have also been employed in aqueous suspensions to utilize binding





resins for mineral fibers, giving valuable resin composites<sup>(921)</sup> and with suitable blowing agents to produce heat-resistant cellular materials.<sup>(922)</sup> Another product in this series called Kerimid 601 is being explored for the production of multilayer printed circuits.<sup>(1111)</sup>

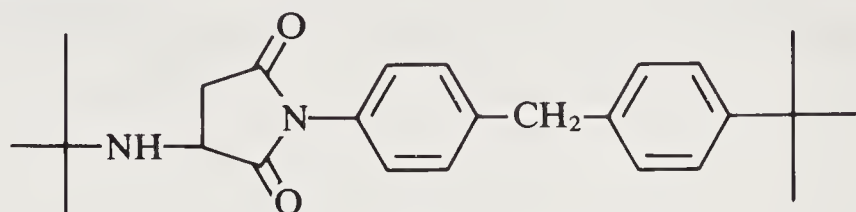
The polymerization kinetics of an equimolar mixture of *N,N'*-hexamethylene-bismaleimide and 4,4'-diamino-diphenylmethane has been explored.<sup>(1116)</sup> Conversion rates for the primary amine groups and the formation of gel fraction, in the reaction at 130–160°C, were proportional to the concentration of primary amine groups raised to the  $4.3 \pm 0.2$  and  $0.97 \pm 0.06$  power, respectively. The corresponding activation energies were  $16.6 \pm 0.7$  and  $40.8 \pm 5.6$  kcal/mol. The data show that during melt polymerization the addition of primary amine groups to the double bond is accompanied by homopolymerization of the maleimide double bond, with both reactions complicated by diffusion phenomena. The above chemistry has been employed with tris(4-aminophenyl) phosphate and tris(4-aminophenyl) thiophosphate to give phosphorus containing moldings, exhibiting high softening points.<sup>(923)</sup>

Aniline-formaldehyde condensation products, when treated with MA may be used to prepare polyfunctional maleimides.<sup>(924–927)</sup> After curing, under heat and pressure, these materials exhibit high flexural strength, high shear modulus, and excellent solvent and heat resistance.

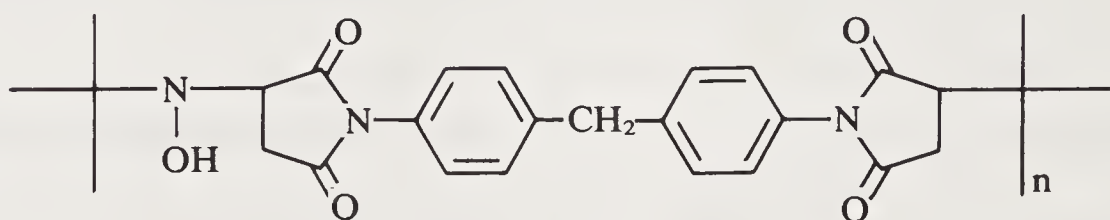
The imides prepared from the cyclopentadiene and methylcyclopentadiene adducts of MA and diamines are useful plasticizers for polyimide resins.<sup>(928,929,1114)</sup> Thermal polymerization of these bisimides also occurs, with the reaction proceeding via double bond cleavage of the cycloaliphatic ring.<sup>(930)</sup> In this case, rates of polymerization are much slower than cure of the bis-maleimides.

Condensation polymerization of equimolar amounts of a diamine with MA is also known to be useable for preparing heat-hardenable resins with succinimide moieties.<sup>(931,932,1104)</sup> For example, condensation of 4,4'-

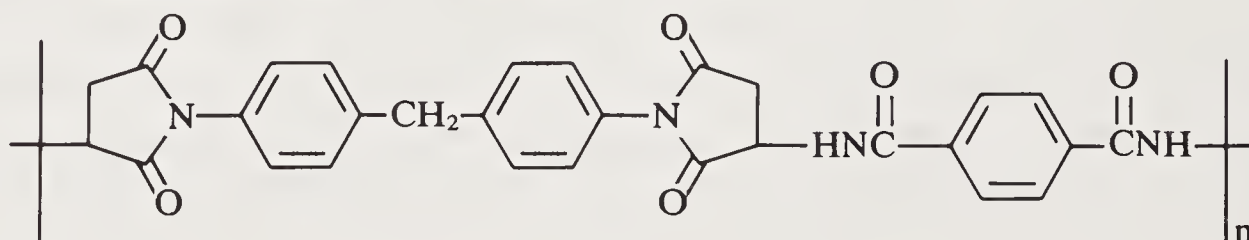
diamodiphenylmethane with MA for 1 h at 175°C gave a polymer with the following structural unit:



Bismaleimides may also be treated with hydroxylamine,<sup>(933)</sup> dicarboxylic acids,<sup>(934)</sup> aminophenols,<sup>(935)</sup> alkenylphenols,<sup>(1000,1124)</sup> phenolics with two or more OH residues,<sup>(1102)</sup> triazene resins,<sup>(1110)</sup> hydrogen sulfide, bisthiols or polythiols,<sup>(936-938,1096,1101,1126,1139)</sup> organocyanates, such as 2,2-bis(4-cyanatophenyl) propane,<sup>(998,1115)</sup> and dicyandiamide<sup>(1113)</sup> and various activated methylene compounds<sup>(1141)</sup> to give chain-extended and/or crosslinked, heat-resistant fabricated products. One of the hydroxyl-amine copolymers, which may be fabricated into laminates and moldings at 150–300°C, is reported to have the following simplified structure.

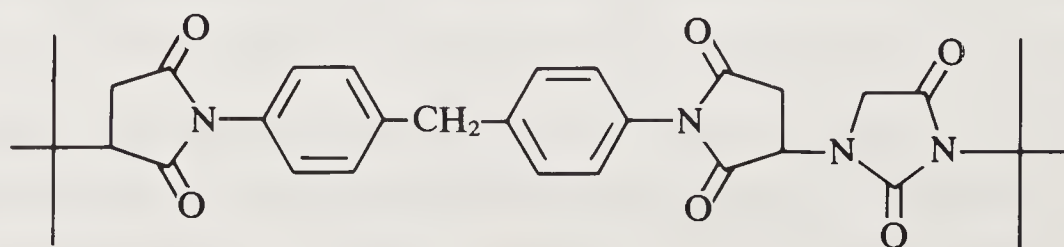


Poly(amide-imides) may be prepared from polyaddition reactions of dialdoximes with bismaleimides,<sup>(939)</sup> with an example of the structure shown from polycondensation of terephthaldoxime with *N,N'*-[4,4'-diphenyl(methane)] bismaleimide.



The amide-imide copolymer could be fabricated into films having high tensile strengths, elongation of 1.0–4.7%, and stable to 250°C.<sup>(939)</sup>

In the presence of tertiary amines, bismaleimides will undergo polyaddition reaction with hydantoin, bishydantoins,<sup>(940)</sup> or thio-hydantoins<sup>(1102)</sup> to give moldings and laminates with good heat resistance, mechanical and electrical properties. It is assumed that resin prepared from *N,N'*-[4,4'-diphenyl(methane)] bismaleimide and hydantoin has the following structural unit.



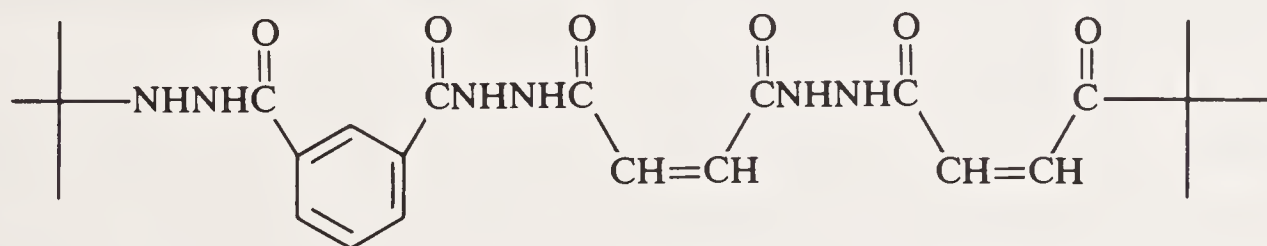


Polycondensation reactions between MA and 1,1',3,3'-tetrakis(4-aminophenyl)-2,2'-biimidazolidinylidene is claimed to produce a photoconductive polymer, with a unique charge-transfer complex structure.<sup>(941)</sup>

Condensation reactions between bismaleimides and various furfuryl derivatives<sup>(942,943,1100)</sup> can be used to prepare nonflammable foams, coatings, and molded plastics. Aldimine-MA polycondensation reactions may also be used to obtain coatings and structural foams.<sup>(944)</sup> For example, polycondensation of bis[4-(benzylideneamino)phenyl] methane with MA, in the presence of a blowing agent, gives chemical- and heat-resistant foams. Thermosetting mixtures for heat-resistant powder coatings may be prepared from blends of bismaleimides with azomethines.<sup>(945)</sup> The mixture may be stored for long periods but crosslink on heating at 100–280°C. Blends of polyfunctional cyanic esters, bismaleimides, and polyesters may also be crosslinked with heat for coatings applications.<sup>(947)</sup> Tough, transparent, heat-resistant films are obtained from polycondensation reactions between bismaleimides and 2,5-dialkyl-3,4-diarylcyclopentadienone,<sup>(946)</sup> with CO elimination as the reaction progresses.

Heat-curable imide resins are prepared by condensation reaction of bismaleimides with dicarboxylic acid dihydrazides.<sup>(1097,1098)</sup> In the reaction, the bismaleimides are coupled with the dihydrazides via a Michael-type reaction between the active primary hydrogen-nitrogen residues and the double bond on the maleimides.

Polyaddition reactions also readily occur between *N,N'*-bisisomaleimides and diamines or dihydrazides to give linear unsaturated poly(amide-hydrazides) or poly(hydrazides).<sup>(948–950)</sup> For example, polycondensation of *N,N'*-bisisomaleimide and isophthaloyldihydrazide, in dimethylsulfone at room temperature, gave the polyhydrazide shown below. It appears that this reaction does not progress to give a polymer of sufficiently high molecular weight to be of commercial interest.



Blends of bismaleimides with poly(betaamino crotononitrile) are storage stable materials, converted with heat to thermosetting compositions useful as coating and laminating resins.<sup>(1122)</sup>

## 12.11. MISCELLANEOUS MA CONDENSATIONS

Resinous products prepared from hexakis(methoxyl methyl) melamine-MA,<sup>(951)</sup> urea-formaldehyde,<sup>(952)</sup> and hydroxyalkyl-substituted urea-MA reactions<sup>(953)</sup> have received some attention in coatings and moldings.

Water-soluble amino condensation products, with maleate carboxyl residues show possible utility in photographic applications.<sup>(954)</sup>

Phenol-formaldehyde,<sup>(955)</sup> aniline-formaldehyde,<sup>(956)</sup> diphenyl oxide-formaldehyde,<sup>(957)</sup> trioxane,<sup>(958)</sup> tetrahydrofuran,<sup>(959)</sup> formaldehyde,<sup>(960)</sup> and formaldehyde-ketene<sup>(961)</sup> have been combined with MA to give resinous materials. The reaction between the trioxane and formaldehyde-ketene was initiated by various types of radiation.

In addition to epoxy resins, MA has been investigated as a crosslinker for a variety of polymers. For example, poly(oxycyclohexene),<sup>(962)</sup> polyarylates,<sup>(963,969)</sup> hydroxy-substituted polyspiro resins,<sup>(964,965)</sup> and polymethylsiloxanes<sup>(966)</sup> have been crosslinked with MA to give thermoplastic adhesives, heat-resistant polyarylates, electrical insulating materials, and other composites.

Condensation reactions between hydroxyethyl cellulose or carboxy methyl hydroxy-ethyl cellulose provides potentially useful textile sizing resins.<sup>(966)</sup> Starch materials have been treated with MA to obtain starch with maleate half-ester residues, with a substitution degree of 0.01–3.00.<sup>(1125)</sup> Styrene monomer is grafted onto the maleate/fumarate residues, with high efficiency, using standard free-radical initiators.

A number of patents<sup>(967–971)</sup> describe how ethylenimine, *N*-phenylaziridine, *N*(2-cyanoethyl) aziridine, bis and trisaziridinyl compounds,<sup>(972)</sup> as well as *N*-acetylaziridine,<sup>(973)</sup> undergo polycondensation reaction with MA to provide adhesives, coatings, and laminates. The ethylenimine-MA reaction is highly exothermic; however, the reaction may be controlled in solution to obtain low-molecular weight polyamides, exhibiting a glass transition temperature ( $T_g$ ) of 150–200°C and melting points greater than 200°C. Aziridines are also highly effective crosslinkers for acid-terminated polyesters.<sup>(974)</sup>

Polyethylenimine resins, when treated with MA, give resinous materials suitable for paper stock modification, rust inhibitors, acid electroplating resins, textile finishing agents and other uses.<sup>(975–979)</sup>

Block polyamide-polyesters have been obtained by treating amine-terminated polyamides with MA and glycols.<sup>(980)</sup> When cured with melamine derivatives, these materials are claimed for attractive coatings.<sup>(980)</sup> It has been reported that MA-diamine reactions may be used to prepare unsaturated polyamides,<sup>(981)</sup> which are crosslinkable by UV light. Carothers<sup>(982)</sup> was one of the first to explore this type of unsaturated polyamides. Interfacial polycondensation reactions between fumaroyl dichloride and diamines provides polyamides giving tough, infusible films and high modulus fibers, stable to approximately 285°C.<sup>(983,1027,1028)</sup> Pryde<sup>(202)</sup> recently authored a very good review on the subject of unsaturated polyamides.

It is interesting to report here also that dialkyl maleates may be readily epoxidized to give epoxysuccinates (see Chapter 3). These unique epoxides



react with diamines to give soluble, hydrophilic polyamides with epoxy residues.<sup>(984,986)</sup>

Compounds such as 2-methyl-2-oxazoline will undergo polycondensation reactions with MA.<sup>(985)</sup> The water-soluble 1:1 copolymer of 2-methyl-2-oxazoline-MA is potentially useful in adhesive formulations.

The reaction of MA with diisocyanates, in the presence of controlled amounts of water, can be used to prepare foamed products for insulation.<sup>(987)</sup> The reaction is run at  $<150^{\circ}\text{C}$  in the presence of a small amount of foam-stabilizing surfactant, to give a cellular resin of apparent density  $<30\text{ lb/ft}^3$  ( $480\text{ g/l}$ ).

The condensation reaction of aluminum alcoholates with MA has received some study.<sup>(988,989)</sup> Other vinyl monomers, such as methyl methacrylate, may be combined with the mixture. Both addition and condensation reactions occur in such mixtures to give thermosetting resins (see Chapter 9).





# APPENDIX

## PATENT LISTINGS

While every effort has been made to make these patent listings complete and accurate, it is realized that in a compilation of this nature some errors and omissions are almost inevitable. Patents cited in the text are not generally included in this appendix. Many of the patents were screened, but, in some cases the information presented is only what could be obtained from some previous abstractor's interpretation of the patent in question. This is particularly true of foreign patents. No attempt was made to validate the claims or value of the listed patents. It was also hard to assign, in most cases, only one or two uses for the patents, since multiple uses were often claimed. However, the tabulated patents should help the chemist find areas for new polymer design, develop new uses for existing technology, and preclude wasted effort.

- A.1. Terpolymers Containing Maleic Anhydride ( $M_1$ )
- A.2. Maleic Anhydride–Styrene Copolymer Patents
- A.3. Olefin–MA Copolymer Patents
- A.4. Alkyl Vinyl Ether–Maleic Anhydride Copolymer Patents
- A.5. Vinyl Acetate–Maleic Anhydride Copolymer Patents
- A.6. Patents on Maleic Anhydride Copolymers with Miscellaneous Monomers
- A.7. MA Graft Polymer Patents

Table A.1. Terpolymers Containing Maleic Anhydride (M<sub>1</sub>)

Applications	Monomer M <sub>2</sub>	Monomer M <sub>3</sub>	Patent	Year	Assignee
PRODUCTION PROCEDURE					
Production procedure	Styrene	Vinyl acetate	Germany 540,101	1931	I. G. Farben
Production procedure	Styrene	Vinyl acetate	Britain 376,479	1932	I. G. Farben
Production procedures	Styrene	Vinyl acetate	France 719,145	1932	I. G. Farben
Production procedure	Styrene	Vinyl chloride	France 835,357	1938	I. G. Farben
Production procedure moldings	Styrene	N-Methylmaleimide	Britain 505,120	1939	I. G. Farben
Production procedures	Styrene	2-Hydroxyethyl methacrylate	United States 2,340,110	1944	General Electric
Production procedure	Styrene	$\alpha$ -Pinene	United States, 2,383,399	1945	DuPont
Production procedure ion-exchange resin	Styrene	Divinyl benzene	United States 2,471,818	1949	Dow
Production procedure and coatings	Endomethylenephthalic acid esters	Styrene	United States 2,493,343	1950	PPG
Production procedure	Ethylene	1,5-Hexadiene	United States 3,060,155	1962	Monsanto
Production procedure	Ethylene	Diallyl ether	United States 3,073,805	1962	Monsanto
Production procedure	Ethylene	Propylene	United States 3,278,495	1966	Chemische Werke
Production procedure	Ethylene	Dicyclopentadiene	Netherlands 1,207	1966	Farbenwerke Hoechst
Production procedure	Methacrylic acid	Acrylamide	United States 3,414,547	1968	Nalco Chemical
Production procedure	Ethylene	Vinyl acetate	E. Germany 137,443	1979	VEB Leuna-Werke
Production procedure	2,4,4-Trimethyl-1-pentene	2,4,4-Trimethyl-2-pentene	W. Germany 2,840,502	1980	BASF A.G.
Production procedures	Acrylonitrile	Styrene	Japan 78,006	1980	Toray Industries, Inc.
Production procedure	Styrene	Acrylonitrile	Japan 116,712	1980	Mitsubishi-Monsanto
Production procedure, molding resins	Styrene	Acrylonitrile	Japan 125,113	1980	Toray Industries, Inc.
ADHESIVES					
Glass-fiber laminates and adhesives	Ethylene or styrene	Vinyl acetate	United States 2,519,764	1950	DuPont



Metal materials	Vinyl chloride	Vinyl acetate	United States 2,728,703	1955	U.S. Rubber
Specialty	Vinyl chloride	Vinyl acetate	Britain 773,573	1957	Farbwerke Hoechst A.G.
Specialty	Vinyl chloride	Vinyl acetate	W. Germany 1,011,102	1957	Dunlop Rubber
Pressure sensitive	Vinyl acetate	Vinyl sterate	United States 2,913,355	1959	Johnson & Johnson
Metal sheet	Vinyl chloride	Vinyl acetate	W. Germany 1,092,145	1960	Society Phenix Works
Metal to PVC	Vinyl chloride	Vinyl acetate	Britain 864,879	1961	Scott Bader
Epoxy resin hardener	Styrene	Methyl methacrylate	Britain 940,695	1963	Rohm & Haas
Vinyl plastics and adhesives	Vinyl chloride	Vinyl acetate	United States 3,136,657	1964	Air reduction
Pressure sensitive	Butadiene	Styrene	United States 3,156,581	1964	Milky Way Products
	Butadiene	Acrylonitrile			
PVC to metal	Vinyl chloride	Vinyl acetate	United States 3,159,597	1964	Armstrong Cork
Adhesive latex for paper	Acrylonitrile	Butadiene	Belgium 636,527	1964	Milky Way Products
PVC laminating	Vinyl chloride	Vinyl acetate	Belgium 640,999	1964	Solvay & Cie
Packaging film adhesives	Vinyl chloride	Vinyl acetate	United States 3,188,265	1965	3M
Vinyl polymer printing	Vinyl chloride	Vinylidene chloride	Belgium 654,055	1965	Kureha Chemical Industries
Epoxy resin hardener	Styrene	Ethyl acrylate	Britain 994,881	1965	Rohm & Haas
Specialty	Vinyl chloride	Vinyl acetate	Japan 12,995	1965	Kureha Chemical Industries
Laminating resins	Vinyl chloride	Vinyl acetate	Netherlands 14,051	1965	Solvay & Cie
Nonwoven fibrous	Butadiene	Methacrylic acid	United States 3,256,234	1966	International Latex
Pressure sensitive	Octyl acrylate	Vinyl acetate	United States 3,257,478	1966	National Starch
Pressure sensitive	Ethyl acrylate	Vinyl acetate	Netherlands 584	1966	National Starch
Gummed labels	Vinyl chloride	Vinyl acetate	United States 3,296,723	1967	Buntpapierfabrik
Pressure sensitive	2-Ethylhexyl acrylate	Vinyl acetate	France 1,560,639	1969	PPG
Pressure sensitive	Vinyl acetate	2-Ethylhexyl acrylate	W. Germany 1,920,746	1969	National Starch
Films	Vinyl chloride	Vinyl acetate	United States 3,513,055	1970	FMC Corporation
Polyolefins	Vinyl chloride	Vinyl acetate	United States 3,522,126	1970	Continental Can
Pressure sensitive	2-Ethylhexyl acrylate	Vinyl acetate	United States 3,551,391	1970	Johnson & Johnson
Pressure sensitive	2-Ethylhexyl acrylate	Diacetone acrylamide	W. Germany 1,961,615	1970	Johnson & Johnson
Glossy paper	$\alpha$ -Olefins	SO <sub>2</sub>	United States 3,563,961	1971	Dow Chemical
Polyamide heat sealing	Vinyl chloride	Vinyl acetate	United States 3,576,778	1971	National Starch
Magnetic tape	Vinylidene chloride	Acrylonitrile	France 2,071,494	1971	Kodak Pathe

Table A.1 (cont.)

Applications	Monomer M <sub>2</sub>	Monomer M <sub>3</sub>	Patent	Year	Assignee
Emulsion paints and adhesives	Butadiene	Alkyl vinyl ethers	W. Germany 2,105,528	1971	Kansai Paint
General purpose Vinyl	Styrene	Butadiene	W. Germany 2,112,574	1971	Dow Chemical
Polyethylene can liner	Vinylidene chloride	Vinyl acetate	Japan 21,116	1971	Kureha Chemical
Pressure sensitive	Vinyl chloride	Vinyl acetate	United States 3,637,103	1972	Continental Can
Glass fiber	Octyl acrylate	Vinyl acetate	United States 3,677,985	1972	National Starch
	Acrylonitrile	Styrene	W. Germany 2,165,370	1972	Sumitomo Chemical
	Butadiene	Styrene			
Carpet backing	Isobutene	Divinyl benzene	United States 3,720,637	1973	Chevron Research
Pressure sensitive	Vinyl acetate	Octyl acrylate	W. Germany 1,645,063	1973	National Starch
Glass roving	Vinyl chloride	Vinyl acetate	Japan 9,592	1973	Central Glass
Emulsion	Vinyl chloride	2-Ethyl hexyl acrylate	Japan 13,927	1973	Shinetsu Chemical
Pressure sensitive	Alkyl acrylates	Vinyl acetate	Japan 66,636	1973	Nichiban
Polyolefin	Ethylene	Vinyl acetate	Romania 55,738	1973	Grupul Industrial
Pressure sensitive	2-Ethylhexyl acrylate	Dimethyl amino ethyl methacrylate	United States 3,790,533	1974	C. M. Samour
Vinyl	Vinyl chloride	Vinyl acetate	United States 3,809,603	1974	Avery
Vinyl	Vinyl acetate	Vinyl chloride	United States 3,850,786	1974	National Starch
Polyolefin	Isobutylene	Methyl acrylate	W. Germany 2,404,961	1974	Sumitomo Chemical
Epoxy resin modifier	Vinyl acetate	Vinyl chloride	Japan 9,609	1974	Bostic Japan
Metallized polyethylene film	Vinyl acetate	Vinyl chloride	Japan 67,937	1974	Olin
Polyolefins	Isobutylene	Methyl acrylate	Japan 103,983	1974	Sumitomo Chemical
Acrylic	Acrylic acid	1,3-Butadiene	United States 3,867,250	1975	Dow Chemical
Flexible printed circuit	$\alpha$ -Methylstyrene	Styrene	W. Germany 2,410,728	1975	Sumitomo Bakelite
Pressure sensitive	Butyl acrylate	2-Ethylhexyl acrylate	Japan 10,828	1975	Siaden Chemical
Modifier for epoxy adhesives	Vinyl chloride	Vinyl acetate	Japan 150,782	1975	Teijin Ltd.
Vinyl	Vinyl chloride	Vinyl acetate	U.S.S.R. 508,513	1976	—
Hot melt	Ethylene	Acrylamide	United States 4,032,692	1977	Ruhr Chemie A.G.



Polyester films	Vinyl acetate	Vinyl chloride	Japan 46,991	1977	Nitto Electric
Specialty	C <sub>3-20</sub> $\alpha$ -Olefins	Acrylic acid	Netherlands 154,754	1977	Sumitomo Chemical
Hot melt	Ethylene	Vinyl acetate	E. Germany 137,240	1979	VEB Leuna-Werke
Agglomeration resistant adhesive granules	Ethylene	Vinyl acetate	E. Germany 138,985	1979	VEB Leuna-Werke
Hot melt	Ethylene	Vinyl acetate	E. Germany 139,132	1979	VEB Leuna-Werke
Aluminum foil	Vinyl chloride	Vinyl acetate	Japan 111,536	1979	Toyo Aluminum
Adhesives	Pentaerythritol triacrylate	Propylene	Japan 160,449	1979	Showa Denko
Pressure sensitive	2-Ethylhexyl acrylate	Vinyl acetate	United States 4,196,254	1980	Johnson & Johnson
Plastic and film	Ethylene	Vinyl acetate	Japan 13,727	1980	Asahi Chemical
Pressure sensitive	Alkyl acrylate	Vinyl ester	Netherlands 163,531	1980	Ashland Oil
Curable adhesive	Vinyl chloride	Vinyl acetate	West Germany 3,020,699	1981	Lord Corp.
Curable thermoplastic adhesive	Vinyl chloride	Vinyl acetate	United States 4,250,274	1981	Lord Corp.

BOILER SCALE CONTROL AGENT

Boiler scale control agents	$\alpha$ -Methylstyrene	Acrylamide	United States 4,065,607	1977	Pfizer, Inc.
Scale control agents	Acrylamide	Methacrylamide	United States 4,223,120	1980	Pfizer, Inc.
Pipeline scale control resins	Acrylamide	Styrene	Netherlands 166,479	1981	Pfizer, Inc.

CELLULAR MATERIALS

Plastic foams	Acrylamide	Methyl methacrylate	France 1,368,383	1964	Sekisui Chemical
Plastic foams	Acrylamide	Acrylonitrile	Netherlands 3,715	1968	Stamicarbon N.V.
Molded cellular objects	Acrylamide	Acrylic acid	Britain 1,204,608	1970	Rohm & Haas
Hard insulating	Methyl methacrylate	Acrylonitrile	W. Germany 2,047,096	1972	Rohm & Haas
Improved polyurethane foams	Acrylonitrile	Styrene	Europe 6,605	1980	Union Carbide

Table A.1 (cont.)

Applications	Monomer M <sub>2</sub>	Monomer M <sub>3</sub>	Patent	Year	Assignee
COATINGS					
General purpose	Styrene	Vinyl acetate	United States 2,047,398	1936	I. G. Farben
Production procedure	Styrene	Vinyl chloride	France 835,357	1938	I. G. Farben
Crosslinking	Styrene	Bishydroxyethyl fumarate	United States 2,361,019	1944	PPG
Thermosetting resins	Styrene	Endomethylene tetra-hydrophthalic acid	United States 2,479,486	1949	PPG
Production procedure and coatings	Endomethylenephthalic acid esters	Styrene	United States 2,493,343	1950	PPG
Shellac and mica binders	Styrene	Acrylonitrile	United States 2,547,827	1951	Westinghouse Electric
PAN dye improver additive—sheets	Methyl methacrylate	Acrylonitrile	W. Germany 919,140	1954	Rohm & Haas G.m.b.H.
Metal materials	Vinyl chloride	Vinyl acetate	United States 2,728,703	1955	U.S. Rubber
Waterproofing cellophane	Vinyl chloride	Vinyl acetate	Japan 1,093	1955	Dai Nippon Celluloid
Waterproofing cellophane	Vinyl chloride	Ethyl acrylate	Japan 5,093	1956	Dai Nippon Celluloid
Specialty	Vinyl chloride	Vinylidene chloride	Japan 5,893	1956	Kanega Fuchi Chemical
PAN modifier	Acrylonitrile	Methyl methacrylate	W. Germany 1,006,160	1957	Rohm & Haas G.m.b.H.
Cellophane	Ethyl acrylate	Vinyl chloride	Japan 792	1957	Dai Nippon Celluloid
General purpose	Vinylidene cyanide	Vinyl acetate	United States 2,838,476	1958	B. F. Goodrich
General purpose	Vinyl chloride	Vinyl acetate	Belgium 563,669	1958	SOLVIC Society
Cellophane	Isobutene	Vinylidene chloride	Japan 3,191	1958	Dai Nippon Celluloid
Varnishes	Vinyl chloride	Vinyl acetate	Japan 3,737	1958	Fuji Chemical
PVC	Vinyl chloride	Vinyl acetate	United States 2,891,876	1959	Union Carbide
Specialty	Styrene	Allyl alcohol	United States 2,995,535(7)	1959	Monsanto
Waterproofing cellophane	Vinylidene chloride	Vinyl chloride	Japan 2,338	1959	Toa Synthetic Chemicals



Industrial	Allylated urea formal- dehyde	Styrene	Britain 830,751	1960	British Industrial Plastics
Metal, glass, and wood Cellophane moisture proofing	Vinyl chloride	Vinyl acetate	Britain 837,397	1960	SOLVIC Society
	Vinyl chloride	Vinyl acetate	Britain 844,509	1960	Dainipon Transparent Paper
Electrophotographic	Vinyl chloride	Vinyl acetate	Belgium 599,628	1961	Gevaert Photo Producten N.V.
Book cover coatings General purpose	Vinyl chloride	Vinyl acetate	United States 3,041,222	1962	DuPont
	Styrene	Ethyl acrylate	United States 3,048,552	1962	DuPont
Production procedure	Ethylene	1,5-Hexadiene	United States 3,060,155	1962	Monsanto
Rosin-type resins	Styrene	1,5,9-Cyclododecatriene	W. Germany 1,125,916	1962	Chemische-Werke Huels
Glass	Vinyl sterate	Vinyl triethoxysilane	United States 3,108,920	1963	Brockway Glass
Metal	Vinyl chloride	Vinyl acetate	Belgium 624,775	1963	Imperial Chemical
Wood coatings	Vinyl chloride	Vinyl acetate	Belgium 626,717	1963	Imperial Chemical
Photographic films	Vinyl chloride	Vinyl acetate	Britain 925,069	1963	DuPont
Epoxy resin hardener	Styrene	Methyl methacrylate	Britain 940,695	1963	Rohm & Haas
Metal	Methyl methacrylate	Ethyl acrylate	Britain 942,947	1963	Vinyl Products Ltd.
Photographic films	Vinyl chloride	Vinyl acetate	W. Germany 1,153,249	1963	Agfa A.G.
General purpose	Styrene	Ethyl acrylate	United States 3,154,598	1964	Milky Way Products
Photographic stripping films	Vinyl chloride	Vinyl acetate	Belgium 643,094(5,6)	1964	Gavert Photo Producten N.V.
Specialty	Ethyl acrylate	Vinyl toluene	France 1,381,384	1964	DeSoto Chemical
Air cured	Acrylic acid	Butyl acrylate	United States 1,184,440	1965	W. R. Grace
Epoxy resin hardener	Styrene	Ethyl acrylate	United States 3,196,120	1965	DuPont
Specialty	Vinyl acetate	Vinyl chloride	United States 3,214,286	1965	M & T Chemical
PVC	Vinyl chloride	Vinyl acetate	United States 3,219,475	1965	Cumberland Chemical
Specialty	Butyl acrylate	Acrylic acid	Britain 1,000,218	1965	W. R. Grace
Ferrous metal	C <sub>4</sub> -C <sub>6</sub> Olefins	Styrene	Germany 1,198,473	1965	Esso Research
Antistatic for polyolefins	Vinyl chloride	Vinyl acetate	Japan 13,268	1965	Toyo Rayon
Emulsion	Styrene	Butadiene	United States 3,267,061	1966	Union Carbide
Heat resistant	Butyl acrylate	Styrene	France 1,464,337	1966	DeSoto Chemical
Thermosetting	Butyl vinyl ether	Diethyl maleate	Netherlands 4,305	1966	CIBA Ltd.
Photographic	Ethyl vinyl ether	Methyl acrylate	United States 3,312,554	1967	Eastman Kodak
Antistatic	Vinyl chloride	Vinyl acetate	France 1,474,176	1967	Adhesives-Tapes Ltd.

Table A.1 (cont.)

Applications	Monomer M <sub>2</sub>	Monomer M <sub>3</sub>	Patent	Year	Assignee
Thermosetting Specialty	Methyl methacrylate	Vinyl toluene	France 1,476,215	1967	Rohm & Haas
Melamine-cured	Vinyl toluene	Ethyl acrylate	France 1,485,575	1967	DeSoto Chemical
Thermosetting	Butyl acrylate	Styrene	France 1,492,374	1967	Chemische-Werke-Albert
Specialty	Acrylamide	Styrene	Britain 1,123,425	1968	Japan Paint
Specialty	Vinylidene chloride	Acrylonitrile	Britain 1,131,930	1968	Solvay & Cie
Emulsion type	Vinylidene chloride	Acrylonitrile	France 1,541,556	1968	Solvay & Cie
General purpose	Vinyl chloride	Vinyl acetate	France 1,543,838	1968	Imperial Chemical
Thermosetting	Methyl methacrylate	Butyl acrylate	France 1,546,484	1968	Reichhold Chemie
PVC modifier	Methyl methacrylate	Glycidyl methacrylate	France 1,550,216	1968	Balm Paints
Heat sealable polyolefins	Vinyl chloride	$\alpha$ -Olefins	Japan 8,820	1968	Toyo Koatsu Industrial
Thermosetting	Vinyl chloride	Vinyl acetate	United States 3,459,591	1969	Daicell
Film	Styrene	Butyl acrylate	Austria 276,773	1969	Vianova Kunstharz
Thermosetting	Vinyl chloride	Vinyl acetate	Britain 1,263,943	1969	Ciba-Geigy
	Styrene	$\beta$ -Hydroxyethyl methacrylate	Japan 11,266	1969	Toyo Rayon
Water repellent	Vinylidene chloride	Ethylene	Japan 15,197(8)	1969	Mitsui Toatsu Chemicals
Melamine cured	Ethyl acrylate	Methyl methacrylate	Japan 20,227	1969	Mitsubishi Rayon
Thermosetting	Alkyl acrylates	Glycidyl methacrylates	South Africa 7,083	1969	Beiersdorf A.G.
Film	Vinyl chloride	Vinyl acetate	United States 3,507,685	1970	FMC Corp.
Polyester modifier	Vinyl chloride	Vinyl acetate	United States 3,520,844	2970	Sherwin-Williams
Thermosetting metal	Cyclohexyl acrylate	Allyl glycidyl ether	United States 3,527,738	1970	Dow Chemical
Magnetic tape	Vinylidene chloride	Acrylonitrile	United States 3,547,693	1970	Eastman Kodak
Thermosetting	Styrene	Alkyl acrylates	Britain 1,182,225	1970	Coates Brothers
Specialty	Ethyl acrylate	Acrylamide	Britain 1,192,359	1970	Styrene Copolymers Ltd.
Cold setting	Methyl methacrylate	2-Ethylhexyl acrylate	Britain 1,210,966	1970	Japan Gas-Chemicals
Powder	Vinyl chloride	Vinyl acetate	W. Germany 1,917,829	1970	ARFA Roehrenwerke
General purpose	Ethyl methacrylate	Styrene	W. Germany 1,927,460	1970	Th. Goldschmidt A.G.
Specialty	Butyl methacrylate	Methyl methacrylate	Hungary 901	1970	Budalokk Fertekes Mugyantogyar
Antistatic	Methyl methacrylate	Styrene	Japan 18,307	1970	Research Institute Prod- uct Development



Autoxidative air drying	Methyl methacrylate	Styrene		South Africa 6,905	1970	Balm Paints
Nonaqueous dispersion type	Glycidyl methacrylate	Methyl methacrylate		South Africa 6,907	1970	Balm Paints
Glossy paper	$\alpha$ -Olefins	SO <sub>2</sub>		United States 3,563,961	1971	Dow Chemical
Electrocoating resins	Butyl acrylate	Styrene		United States 3,585,172	1971	Ishihara Mining and Chemical
Resins for high-speed electrophotography	Ethyl acrylate	$\beta$ -Hydroxyethyl methacrylate		United States 3,595,647	1971	Ricoh
Metal primer	Vinyl chloride	Vinyl acetate		Britain 1,218,170	1971	Kansai Paint
Electrophotographic films	Vinyl chloride	Vinyl acetate		Britain 1,254,217	1971	Matsushita Electric
Glossy, aqueous paints	Ethyl acrylate	Vinyl acetate		Britain 1,255,482	1971	British Paints
Metal	Methyl methacrylate	Hydroxypropyl methacrylate		France 2,037,215	1971	Deutsch Gold und Silber
Room-temperature curing	Methyl methacrylate	Ethyl acrylate		France 2,041,331	1971	Japan Gas-Chemical
Thermosetting films	Methyl methacrylate	Glycidyl methacrylate		France 2,072,888	1971	Th. Goldschmidt A.G.
Transparent, thermo-setting	Acrylic acid	Glycidyl methacrylate		W. Germany 1,961,452	1971	Th. Goldschmidt A.G.
Electrophotographic Powder	Vinyl acetate	Vinyl versatate		W. Germany 2,017,019	1971	DeSoto
Emulsion paints and adhesives	Ethyl acrylate	Butyl methacrylate		W. Germany 2,064,916	1971	Mitsui Toatsu Chemical
Heat sealing polyolefins	Butadiene	Alkyl vinyl ethers		W. Germany 2,105,528	1971	Kansai Paint
General purpose	Vinyl chloride	Acrylonitrile		Japan 1,114	1971	Daicell
	Styrene	Butyl acrylate		Japan 10,951	1971	Dainippon Ink and Chemicals
Water soluble	Ethyl acrylate	Styrene		Japan 19,437	1971	Dainippon Ink and Chemicals
Thermosetting Polyolefins	Acrylamide	Styrene		Japan 21,649(50)	1971	Japan Paint
	Ethylene	Vinyl acetate		Romania 52,457	1971	Romania “Petrochemic”
Antistatic	Vinyl chloride	Vinyl acetate		United States 3,634,336	1972	Eastman Kodak
Flexible, water-resistant films	<i>N</i> -Vinylpyrrolidone	Ethyl acrylate		United States 3,652,481	1972	GAF
Acrylic latex coagulants	Butyl acrylate	Methacrylic acid		United States 3,677,991	1972	Dow Chemical
Specialty	<i>N</i> -Vinyl pyrrolidinone	2-Ethylhexyl maleate		United States 3,686,150	1972	GAF

Table A.1 (cont.)

Applications	Monomer M <sub>2</sub>	Monomer M <sub>3</sub>	Patent	Year	Assignee
Electrophoretic	Ethyl acrylate	Acrylamide	W. Germany 2,065,135	1972	Toa Gosei Chemical
Electrophoretic	Butyl acrylate	Hydroxyethyl methacrylate	W. Germany 2,118,692	1972	Takeda Chemical
Glass fiber	Acrylonitrile	Styrene	W. Germany 2,165,370	1972	Sumitomo Chemical
Vinyl	Butadiene	Styrene			
Polymeric pigment binders	Vinyl chloride	Vinyl acetate	Japan 18,983	1972	Toray
	Styrene	Divinyl benzene	Japan 21,233	1972	Tokuyama Soda
Thermosetting	Styrene	Ethyl acrylate	Japan 25,470	1972	Showa Polymer
Cement emulsion	Vinyl chloride	2-Ethylhexyl acrylate	Japan 38,527	1972	Shin Etsu Chemical
Thermosetting	Butyl acrylate	Styrene	Japan 42,159	1972	Mitsubishi Rayon
Photocurable	Styrene	Acrylonitrile	United States 3,715,211	1973	Horizons Inc.
Powder	Butyl methacrylate	Glycidyl methacrylate	W. Germany 2,240,260	1973	Ford-Werke A.G.
Powder	Styrene	Glycidyl methacrylate	W. Germany 2,240,314	1973	Ford-Werke A.G.
Vinyl	Butyl acrylate	Methyl methacrylate	W. Germany 2,263,874	1973	Mitsubishi Gas-Chemical
Sponge leather modifier	Acrylic acid	Steryl methacrylate	Japan 5,005	1973	Toyo Cloth
Thermosetting	Methyl methacrylate	2-Ethylhexyl acrylate	Japan 8,264	1973	Mitsubishi Rayon
Vinyl	Methyl acrylate	Vinylidene chloride	Japan 8,452	1973	Kureha Chemical
Glass roving	Vinyl chloride	Vinyl acetate	Japan 9,592	1973	Central Glass
Photosensitive	Methyl methacrylate	Glycidyl methacrylate	Japan 10,185	1973	Fuji Photo Film
Specialty	Methyl methacrylate	2-Vinylpyridine	Japan 14,413(4)	1973	Mitsubishi Rayon
Vinyl	Vinyl acetate	Vinyl chloride	Japan 19,549	1973	Kuraray
Vinyl	Acrylonitrile	Butyl acrylate	Japan 22,167	1973	Mitsubishi Rayon
Vinyl	Acrylonitrile	Alkyl acrylates	Japan 37,568	1973	Mitsui Toatsu Chemical
Waterproofing	Methyl methacrylate	Vinyl acetate	Japan 39,215	1973	Nippon Synthetic Chemical
Electrophoretic	Butyl acrylate	Styrene	United States 3,798,193	1974	American Cyanamid
PVC	Methyl methacrylate	Butyl acrylate	France 2,216,913	1974	Nippon Oils and Fats



Thickeners	Styrene	Vinyl benzyl ether	W. Germany 2,333,301	1974	Dow Chemical
Antistatic agents	1-Decene	SO <sub>2</sub>	W. Germany 2,333,323	1974	DuPont
Electrophotographic binders	Ethyl acrylate	Methacrylic acid	W. Germany 2,336,338	1974	Mitsubishi Paper Mills
Photographic films	Vinyl chloroacetate	Methyl methacrylate	W. Germany 2,357,356(7)	1974	Imperial Chemical
Crosslinkable PVC	Vinyl acetate	Vinyl chloride	W. Germany 2,364,057	1974	Hooker Chemical
Photographic diffusion transfer	Methyl methacrylate	Divinyl benzene	W. Germany 2,364,740	1974	Polaroid
Water-soluble	1-Hexene	Styrene	W. Germany 2,413,922	1974	Toray Industries, Inc.
Vinyl	Methyl methacrylate	Butyl acrylate	Japan 2,730	1974	Nippon Oils and Fats
PVC	Butyl acrylate	Vinyl acetate	Japan 4,056	1974	Nippon Zeon
Electrophotographic binder resins	Styrene	Butyl methacrylate	Japan 90,937	1974	Fuji Photo Film
Vinyl	Vinyl acetate	Vinyl chloride	Japan 92,148	1974	Mitsubishi Rayon
Rustproofing for steel	<i>N</i> -Vinylpyrrolidone	Styrene	Japan 99,533	1974	Kocho Ryo
Electrophotographic binder	Ethyl acrylate	Methyl methacrylate	Japan 109,039	1974	Mitsubishi Paper Mills
PVC antifogging	Methacrylic acid	Methyl methacrylate	Japan 116,180	1974	Sakai Chemical
Leather articles	Vinyl chloride	Vinyl acetate	Japan 120,976	1974	Dainichiseika and Chemicals
Polystyrene laminates	Vinylidene chloride	Styrene	Japan 121,890	1974	Sumitomo Chemical
Photocurable	Isobutyl methacrylate	Glycidyl methacrylate	Netherlands 8,103	1974	Kansai Paint
Microorganism resistant	Tributyltin methacrylate	Vinyl acetate	Netherlands 9,239	1974	Australian Commonwealth
Thermosetting emulsion	Acrylamide	Ethylene	United States 3,875,100	1975	Charles S. Tanner
Electrostatic powder	Butyl methacrylate	Methyl methacrylate	United States 3,888,943	1975	Ford Motor
Waterproofing agents	Styrene	SO <sub>2</sub>	United States 3,890,287	1975	Dow Chemical
Water emulsifiable anionic resins	Butyl acrylate	Styrene	United States 3,917,573	1975	American Cyanamid
Antifouling steel	Methyl methacrylate	Styrene	Britain 1,408,327	1975	Nippon Oils and Fats
Vinyl	Vinyl acetate	Vinyl chloride	W. Germany 2,409,800	1975	Chemische Werke Huels
Powder	Methyl methacrylate	Styrene	W. Germany 2,433,450	1975	Union Chimique
Powder	Alkyl acrylates	Alkyl methacrylate	W. Germany 2,454,827	1975	Ford-Werke A.G.
Powder	Butyl methacrylate	Methyl methacrylate	W. Germany 2,457,826	1975	Ford-Werke A.G.

Table A.1 (cont.)

Applications	Monomer M <sub>2</sub>	Monomer M <sub>3</sub>	Patent	Year	Assignee
Powder	Butyl methacrylate	Styrene	W. Germany 2,457,894	1975	Ford-Werke A.G.
Thermosetting	Ethyl acrylate	Styrene	W. Germany 2,509,237	1975	Rohm & Haas
Powder	Butyl methacrylate	Glycidyl methacrylate	W. Germany 2,509,410	1975	Ford-Werke
Photosensitive	Myristyl methacrylate	Styrene	Japan 70,023	1975	Sanyo Chemical
Radiation curable	Glycidyl acrylate	2-Hydroxyethyl acrylate	Japan 10,119	1975	Mitsubishi Rayon
Metal	Methyl methacrylate	2-Hydroxyethyl acrylate	Japan 112,426	1975	T. Ohta
Polyurethane modified	Isobutylene	Methyl acrylate	Japan 148,503	1975	Sumitomo Chemical
Modifier for epoxy adhesives	Vinyl chloride	Vinyl acetate	Japan 150,782	1975	Teijin Ltd.
Thermoreactive films	Butyl acrylate	Glycidyl acrylate	U.S.S.R. 489,762	1975	—
Electrocoating resins	Alkyl acrylates	Styrene	United States 3,984,382	1976	American Cyanamid
Powder	Vinyl chloride	Vinyl acetate	United States 3,988,493	1976	DuPont
Molding resins	Isobutylene	Ethyl acrylate	Britain 1,476,765	1977	Exxon Research
Fire retardant	Styrene	Bromoneopentyl methacrylate	W. Germany 2,659,174	1977	Monsanto
Self-crosslinking	Vinyl acetate	Dimethylvinylethynyl <i>t</i> -butylperoxide	U.S.S.R. 619,488	1978	—
Photographic films	Styrene	Acrylamide	United States 4,172,732	1979	Fuji Photo
Photographic film timing layers	Ethylene	Propylene	Britain 2,018,450	1979	Fuji Photo
	Propylene	Ethylene			
	Vinyl chloride	$\alpha$ -Olefin			
	Styrene	$\alpha$ -Olefin			
	Vinyl ethers	$\alpha$ -Olefin			
Rubber and fabrics	Styrene	Butadiene	E. Germany 137,718	1979	Chemische-Werk Huels
Photosensitive compositions	Butadiene	Olefin	W. Germany 2,720,228	1979	Japan Synthetic Rubber
Road marking pigment binders	Styrene	Isobutyl acrylate	W. Germany 2,749,625	1979	BASF A.G.
Tinplate food container	Vinyl acetate	Vinyl chloride	W. Germany 2,838,383	1979	Union Carbide
Emulsion thickeners	Methacrylic acid	Butadiene	Japan 34,035	1979	Chemische-Werk Huels



Emulsion Vinyl	Styrene	Alkyl methacrylates	Japan 37,244	1979	Dainippon Ink
Impact-resistant protective coatings	Methyl methacrylate	Vinyl acetate	Japan 41,990	1979	Shinto Paint
Calcined ti slag	Vinyl acetate	Vinyl chloride	Japan 52,136	1979	Nippon Paint
Transparent, printable coatings	Styrene	Itaconic acid	Japan 77,294	1979	—
Emulsion, metal	Vinyl acetate	Vinyl chloride	Japan 92,811	1979	—
Thermosetting metallic paints	Vinyl acetate	Vinyl chloride	Japan 96,550	1979	Union Carbide
Waterproof materials	Styrene	Hydroxyalkyl methacrylate	Japan 116,037	1979	Dainippon Ink
Coatings	Vinyl chloride	Methyl acetate	Japan 130,630	1979	Nippon Synthetic Chemical
Thermosetting for metal	Ethylene	Vinyl acetate	Japan, 155,242	1979	Nippon Petrochemicals
Photographic film	Vinyl acetate	Vinyl chloride	Europe 11,883	1980	Metallgesellschaft A.G.
Powder coating binders	Styrene	Vinyl acetate	W. Germany 2,310,469	1980	Konishiroku Photo
Vinyl	Methyl methacrylate	Styrene	W. Germany 2,916,256	1980	BASF A.G.
Emulsion	Methyl methacrylate	$\alpha$ -Methylstyrene			
Vinyl	Vinyl chloride	Vinyl acetate	Japan 5,781	1980	Denki Kagaku Kogyo
Photochemical, peelable	Alkyl methacrylates	Styrene	Japan 23,569	1980	Japan Synthetic Rubber
Metal can	Vinyl chloride	Vinyl acetate	Japan 27,319	1980	Denki Kagaku Kogyo
Nonwoven fibrous mat	Vinyl acetate	Methyl acrylate	Japan 43,030	1980	Shinto Toryo
	Vinyl acetate	Vinyl acetate	Japan 80,476	1980	Canon K.K.
	Vinyl acetate	Vinyl chloride	Japan 89,363	1980	Tokyo Ink
	Vinyl acetate	Vinylidene chloride	U.S.S.R. 742,505	1980	Institute of Nuclear Power
Photocurable materials	Styrene	Methacrylic acid	U.S.S.R. 744,425	1980	Chemical Industry Research

COMPOSITES

Polymer-wood	Acrylonitrile	Methyl methacrylate	Britain 1,249,581	1971	Lonza
Heat resistant	$\alpha$ -Methylstyrene	Acrylonitrile	Japan 116,712	1980	Mitsubishi

CONTROLLED-RELEASE POLYMERS

Plant growth regulator carrier	Acrylamide	Methacrylic acid	United States 3,360,356	1967	Nalco Chemical
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Table A.1 (cont.)

Applications	Monomer M <sub>2</sub>	Monomer M <sub>3</sub>	Patent	Year	Assignee
<i>COSMETIC ADDITIVES</i>					
Cosmetic thickening	Ethoxylated lanolin allyl ether	Methyl vinyl ether	Britain 1,273,552	1952	Imperial Chemical
<i>DETERGENT ADDITIVES</i>					
Adhesives and detergent thickener	<i>p</i> -Nonylphenyl allyl ether	Methyl vinyl ether	France 1,541,974	1968	Imperial Chemical
Detergent thickener	Alkyl vinyl ether	Vinyl ether of polyether	United States 3,499,876	1970	GAF Corp.
Detergent builder, sequestering agent	Alkyl vinyl ethers	Diketene	United States 4,009,110	1977	Ciba-Geigy
<i>DISPERSANTS/EMULSIFIERS</i>					
Thickening agent	Vinyl acetate	Divinyl ether	United States 2,640,039	1953	Hawley Products
Polymeric emulsifiers	Allylsucrose	Vinyl alkyl ethers	Britain 800,001	1958	B. F. Goodrich
Clay beneficiation agent—well drilling additive	Ethylene	Diallyl ether	United States 3,070,544	1962	Monsanto
Silver halide dispersant—photographic films	Methacrylic acid	Vinyl acetate	Britain 1,220,246	1971	Konishiroku Photo
Photographic silver halide dispersant	Acrylamide	Vinylpyridine	W. Germany 2,012,970	1971	Mitsubishi Paper Mills
Pigment dispersant	Styrene	Alkyl maleate	United States 3,665,060	1972	Monsanto
Novel dispersants	Alkenylbenzyl ethers	Styrene	United States 4,151,341	1979	Dow Chemical
Polymeric dispersant	Vinyl acetate	Vinyl chloride	Belgium 874,769	1979	Union Carbide
Polymeric dye dispersants	Styrene	Acrylic acid	W. Germany 2,734,204	1979	BASF A.G.
Paint pigment dispersants	Isobutyl acrylate	Styrene	W. Germany 2,841,540	1980	BASF A.G.



ELASTOMERS

Vinyl elastomers	Ethyl acrylate				
	Butadiene				
Rubbers and moldings	Butadiene				
	Ethyl acrylate				
Thermoset	Ethylene				
Thermoplastic	Styrene				
Rubber modifier mold- ing resins					
Moldable rubber blends	Butadiene				
Moldable rubber blends	Styrene				
Moldings	Styrene				
Vulcanizable	Alkyl acrylate				

ENZYME CARRIER RESINS

Enzyme binder (carrier)	Ethyl vinyl ether				
Enzyme binder (carrier) resins	Tetraethylene glycol dimethacrylate				
Enzyme carrier resins	Styrene				

FIBERS/FABRICS

Dye assist agents	Acrylonitrile				
	Acrylic acid				
Textile sizing					
Nylon textile sizing agent	Acrylic acid				
	Styrene				
Textile sizing resins	Vinyl acetate				
Sizing and thickening agents	Styrene				

Table A.1 (cont.)

Applications	Monomer M <sub>2</sub>	Monomer M <sub>3</sub>	Patent	Year	Assignee
Waterproofing textiles	2-Ethylhexyl acrylate	Trimethylolpropane monoallyl ether	United States 3,268,492	1966	Celanese Corp.
Textile sizing resins	Methyl acrylate	Styrene	Japan 12,076	1966	Gooh Chemical Industry
Nonwoven fabrics	Vinylidene chloride	Vinyl chloride	United States 3,300,431	1967	Takeda Chemical
Specialty fibers	Vinyl fluoride	Vinyl acetate	France 1,504,866	1967	Diamond Alkali
Textile sizing	Styrene	Alkyl maleates	Britain 1,121,664	1968	Dan River Mills
Polypropylene dye assists	Acrylonitrile	Divinyl benzene	Japan, 2,563	1969	Tokuyama Soda
Polypropylene dye assist agents	Styrene	Alkyl vinyl ethers	W. Germany 1,952,947	1970	Uniroyal, Inc.
Nylon textile printing pastes	Methyl acrylate	Styrene	Japan 16,879	1972	Kanebo
Nonwoven textile adhesives	Ethyl acrylate	Vinyl acetate	United States 3,753,842	1973	Deering Milliken
Finishing agents	2-Ethylhexyl acrylate	Isobutylene	Japan 117,798	1974	Sumitomo Chemical
Heat resistant nonwoven fabrics	Vinyl acetate	Vinylidene chloride	U.S.S.R. 742,505	1980	As BELO Nuclear
FILMS					
Packaging	Vinyl acetate	Vinyl chloride	Italy 595,760	1958	SOLVIC Industria
Photographic stripping films	Vinyl chloride	Vinyl acetate	Belgium 643,094(5,6)	1964	Gavert Photo Producten N.V.
Specialty	Butyl acrylate	Acrylic acid	Britain 1,000,218	1965	W.R. Grace
Package materials	Vinyl chloride	Vinyl acetate	United States 3,333,683	1967	Anaconda Aluminum
Heat-sealable polyolefins	Vinyl chloride	Vinyl acetate	United States 3,459,591	1969	Daicell
Resins for high-speed electrophotography	Ethyl acrylate	$\beta$ -Hydroxyethyl methacrylate	United States 3,595,647	1971	Ricoh
Thermosetting films	Methyl methacrylate	Glycidyl methacrylate	France 2,072,888	1971	Th. Goldschmidt A.G.
Crosslinkable PVC	Vinyl acetate	Vinyl chloride	W. Germany 2,364,057	1974	Hooker Chemical
Modified poly(vinylidene chloride)	1,3-Butadiene	2-Ethylhexyl acrylate	Japan 4,824	1974	Asahi Dow



Packaging	Vinyl acetate	Vinyl chloride	Japan 45,184	1974	Aicello Chemical
Laminates, films	Vinyl acetate	Vinyl chloride	Japan 67,977	1974	Olin
Food packaging films	Ethylene	Ethyl acrylate	Japan 101,883	1979	Nippon Petrochemicals
Photographic film base materials	Alkyl acrylates	Acrylic acid	Japan 15,267	1980	Konishiroku Photo
Food packaging	Acrylonitrile	Acrylic acid	Japan 19,260	1980	Idemitsu Industry
Photographic films	Vinyl chloroacetate	Methyl methacrylate	Netherlands 166,133	1981	Imperial Chemical

ION-EXCHANGE MATERIALS

Production procedure—ion exchange resin	Styrene	Divinyl benzene	United States 2,471,818	1949	Dow
Cation exchange resins	Styrene	Methacrylic acid	W. Germany 1,113,570	1957	Farbenfabriken Bayer A.G.
Ion-exchange resins	Styrene	Divinyl benzene			
Cation-exchange resins	Styrene	Ethyl acrylate	United States 2,978,402	1961	Hooker Chemical
Anion-exchange resins	Methyl acrylate	Divinyl benzene	United States 3,557,061	1971	Rohm & Haas
Cation-exchange resins	Vinyl acetate	Divinyl benzene	United States 3,791,866	1974	Rohm & Haas
Ion-exchange resins	Divinyl benzene	Butadienes	U.S.S.R. 423,812	1974	Irkutsk State University
		Glycidyl methacrylate	Japan 20,509	1977	Tokuyama Soda

LAMINATES

Glass fiber laminates and adhesives	Ethylene styrene	Vinyl acetate	United States 2,519,764	1950	DuPont
Impregnating resins	Styrene	Acrylic acid	United States 2,530,983	1950	Westinghouse Electric
Thermoset mica binders	Styrene	Acrylonitrile	United States 2,542,827	1951	Westinghouse Electric
Shellac and mica binders	Styrene	Acrylonitrile	United States 2,547,827	1951	Westinghouse Electric
Molding and laminating resins	Styrene	Allyl alcohol	Britain 911,763	1962	Monsanto
Moldings and laminates	Methyl methacrylate	Styrene	Netherlands 8,167	1965	Imperial Chemical
Laminating resins	Vinyl chloride	Vinyl acetate	Netherlands 14,051	1965	Solvay & Cie
Laminating resins	Vinyl chloride	Acrylic acid	W. Germany 2,351,155	1974	Toyo Soda
Laminates, films	Vinyl acetate	Vinyl chloride	Japan 67,977	1974	Olin
Polystyrene laminates	Vinylidene chloride	Styrene	Japan 121,890	1974	Sumitomo Chemical

Table A.1 (cont.)

Applications	Monomer M <sub>2</sub>	Monomer M <sub>3</sub>	Patent	Year	Assignee
Laminating and molding resins	Styrene	Indene	United States 4,117,218	1978	Standard Oil
Multilayer laminates	Ethylene	Vinyl acetate	E. Germany 137,907	1979	VEB Leuna-Werke
Production procedure—molding resins	Styrene	Acrylonitrile	Japan 125,113	1980	Toray Industries, Inc.
LITHOGRAPHIC PLATES					
Lithographic plate resins	Vinyl acetate	Vinyl chloride	United States 3,544,317	1970	Polychrome Corp.
Resins for electrographic plates	Vinyl acetate	Vinyl chloride	United States 3,905,815	1975	3M
MEMBRANES					
Crosslinked	Methacrylic acid	Divinyl benzene	Britain 1,251,550	1971	Tokuyama Soda
Water desalination	Styrene	Methyl methacrylate	W. Germany 2,044,509	1971	Yarsley Research Lab Ltd.
METAL COMPLEXING AGENT					
Metal complexing resins	Acrolein	Acrylic acid	United States 3,686,145	1972	Deutsche Gold und Silber
Detergent builder sequestering agent	Alkyl vinyl ethers	Diketene	United States 4,009,110	1977	Ciba-Geigy
OIL ADDITIVES					
Pour point depressant, VI improver	Vinyl acetate	3-Methylthiophene	United States 2,615,844	1952	Socony-Vacuum Oil
VI Improver	Vinyl acetate Vinyl acetate	3-Methylthiophene Thiophene	United States 2,671,773	1954	Socony-Vacuum Oil



Lubricating oils	1-Decene or styrene	2-Ethylhexyl vinyl ether	United States 2,710,282(3)	1955	Standard Oil
Lubricating oils	Dodecyl fumarate	Allyl acetate	Britain 807,737	1959	Esso Research
Sludge dispersant	Dodecyl fumarate	Vinyl acetate	Britain 844,984	1960	Esso Research
Lubricating oils	Octadecyl fumarate	Vinyl acetate	Britain 846,508	1960	Esso Research
Lubricating and fuel oils	Alkyl fumarates	Vinyl acetate	Britain 872,053	1960	Esso Research
Lube and fuel oil dispersants	Lauryl fumarate	Vinyl acetate	W. Germany 1,145,290	1963	Esso Research
Nonpolar thickener	Styrene	Ethyl acrylate	United States 3,180,843	1965	Dow Chemical
Lubricating oils	Alkyl fumarates	Vinyl acetate	United States 3,184,413	1965	Esso Research
Lube oils	2-Methyl-5-vinylpyridine	Lauryl methacrylate	United States 3,215,632	1965	Shell Oil
Oil and fuels	Lauryl fumarate	Vinyl acetate	United States 3,227,531(2)	1966	Esso Research
Fuels	Lauryl fumarate	Vinyl acetate	France 1,430,524	1966	Esso Research
Thickener	Dicyclopentadiene	Propylene	France 1,510,303	1968	Farbwerke Hoechst
Lube oils	Methyl methacrylate	Dodecyl methacrylate	France 2,016,379	1970	Sanyo Chemical
Lube oils	Methyl methacrylate	Dodecyl methacrylate	United States 3,651,029	1972	Sanyo Chemical
Detergent additive for fuels	C <sub>15-20</sub> $\alpha$ -Olefins	Allyl 3-sulfanyl ether	United States 3,715,368	1973	Chevron Research
Lube oils	Methyl methacrylate	Dodecyl methacrylate	United States 3,795,614	1974	Sanyo Chemical

PAPER MODIFIERS

Thermoplastic papers	Vinyl chloride	Vinyl acetate	United States 2,899,351	1959	Personal Products Corp.
Clay binder for paper	Vinyl acetate	Alkyl acrylates	United States 3,152,922	1964	Rohm & Haas
Adhesive latex for paper	Acrylonitrile	Butadiene	Belgium 636,527	1964	Milky Way Products
Synthetic paper resins	Acrylamide	Methyl methacrylate	France 1,367,027	1964	Nalco Chemical
Anionic resin—pulp production aid	Acrylamide	Methacrylic acid	France 1,518,535	1968	Nalco Chemical
Paper reinforcement aid	Acrylamide	Styrene	France 1,521,163	1968	American Cyanamid
Paper strength additive	Acrylonitrile	Butadiene	Britain 935,420	1970	Milky Way Products
Paper strength additives	Acrylamide	Styrene	United States 3,660,338	1972	American Cyanamid
Paper strength additives	Acrylamide	Styrene	United States 3,790,514	1974	American Cyanamid
Paper sizing	Styrene	Acrylonitrile	W. Germany 2,407,905	1974	American Cyanamid

Table A.1 (cont.)

Applications	Monomer M <sub>2</sub>	Monomer M <sub>3</sub>	Patent	Year	Assignee
Paper sizing resins	Isobutene	Isoprene	Japan 29,124	1974	Kuraray
Paper sizing resins	Butadiene	Isobutene			
Paper sizing resins	Acrylic acid	Styrene	W. Germany 2,421,826	1975	BASF A.G.
Paper sizing, wet	Styrene	Indene	France 2,304,625	1976	—
strength additives	Styrene	Butyl acrylate	United States 4,083,835	1978	BASF A.G.
	Cyclopentadiene	Acrylonitrile			
	Alkyl acrylates	Acrylic acid			
Cationic paper coatings	Styrene	Ethylene	Japan 66,987	1978	Honshu Paper
Paper sizing	$\alpha$ -Olefins	Vinyl chloride	Netherlands 157,024	1978	Monsanto
Paper sizing	Styrene	Acrylamide	Japan 33,285	1979	Seiko Chemical
Anionic paper sizing agent	Styrene	Acrylic acid	W. Germany 2,502,172	1980	BASF A.G.
Paper sizing	Styrene	Methyl methacrylate	Japan 99,909	1980	Honshu Paper
Paper coatings	Styrene	Methyl methacrylate	Japan 157,611	1980	Sakata Shokai
Paper coatings binder dispersant	Butadiene	Methacrylamide	Europe 26,368	1981	BASF A.G.
Anionic paper sizing	Dicyclopentadiene	Vinylcyclohexene	Europe 26,483	1981	Chem Werke Huls
<i>PLASTICS</i>					
Production procedure—moldings	Styrene	N-Methylmaleimide	Britain 505,120	1939	I. G. Farben
Moldings	Styrene	Chloromaleic acid	United States 2,230,240	1941	U.G.I.
Molding resins	Styrene	Acrylonitrile	United States 2,439,227	1948	Monsanto
PAN dye improver additive—sheets	Methyl methacrylate	Acrylonitrile	W. Germany 919,140	1954	Rohm & Haas G.m.b.H.
Materials with improved optical properties	Acrylonitrile	Methyl methacrylate	Britain 727,827	1955	Rohm & Haas
Moldings	Styrene	Acrylonitrile	Britain 816,618	1959	Diamond Alkali



Molding and laminating resins	Styrene	Allyl alcohol	Britain 911,763	1962	Monsanto
Molding resins	Isobutene	1-Methyl-1-butene	Belgium 631,041	1963	Imperial Chemical
Vinyl plastics and adhesives	Vinyl chloride	Vinyl acetate	United States 3,136,657	1964	Air Reduction
Electrostatic recording binder	Vinyl chloride	Vinyl acetate	Britain 964,880	1964	Gavert Photo Producten N.V.
Epoxy resin hardener	Styrene	Ethyl acrylate	Britain 994,881	1965	Rohm & Haas
Thermoplastic molding resins	Vinyl chloride	Styrene	France 1,401,621	1965	Imperial Chemical
Moldings and laminates	Methyl methacrylate	Styrene	Netherlands 8,167	1965	Imperial Chemical
Molding resins	Methyl methacrylate	Styrene	W. Germany 1,231,013	1966	Rohm & Haas G.m.b.H.
Molding resins	Methyl methacrylate	Styrene	Netherlands 5,289	1966	Rohm & Haas G.m.b.H.
	Methyl methacrylate	Vinyl toluene			
Transparent moldings	2-Methyl-1-pentene	2-Methyl-1-butene	Britain 1,087,075	1967	Imperial Chemical
Transparent plastics—windshields	Isobutene	2-Methyl-1-butene	Britain 1,087,297	1967	Imperial Chemical
Molding resins	Methyl methacrylate	$\alpha$ -Methylstyrene	Japan 31,953	1970	Fujikura Kasei
Laminates and moldings	$\alpha$ -Methylstyrene	Methyl methacrylate	United States 3,676,404	1972	Imperial Chemical
Rubbers and moldings	Butadiene	Acrylonitrile	United States 3,753,959	1973	Japan Synthetic Rubber
	Butadiene	Isobutene			
Castings and moldings	Isobutylene	Ethyl acrylate	Britain 1,476,765	1973	Exxon Research
Molding resins	Acrylonitrile	Butyl acrylate	W. Germany 2,258,541	1973	Japan Catalytic Chemical
Sheet molding materials	Methyl methacrylate	Styrene	Japan 12,855	1973	Toray Industries, Inc.
Molding resins	$\alpha$ -Methylstyrene	Styrene	Japan 70,792	1973	Sumitomo Chemical
Molding resins	Acrylonitrile	Styrene	Japan 88,189	1973	Sumitomo Chemical
Polymer alloys—moldings	Ethylene	Vinyl acetate	W. Germany 2,340,743	1974	VEB Leuna-Werke
Electrophotographic recording material	Vinyl chloride	Vinyl acetate	W. Germany 2,346,803	1974	Agfa-Gevaert
Laminating resins	Vinyl chloride	Acrylic acid	W. Germany 2,351,155	1974	Toyo Soda
Molding resins	Methyl methacrylate	$\alpha$ -Methylstyrene	Japan 10,156	1974	Kanegafuchi Chemical
Thermoplastic molding resins	Acrylonitrile	Styrene	Japan 28,693	1974	Mitsui Petrochemical
Molding resins	Acrylonitrile	Styrene	E. Germany 113,922	1974	—

Table A.1 (cont.)

Applications	Monomer M <sub>2</sub>	Monomer M <sub>3</sub>	Patent	Year	Assignee
Molding resins	Styrene	Acrylonitrile	Japan 123,180	1975	Sumitomo Chemical
	$\alpha$ -Methyl styrene	Acrylonitrile			
Molding resins	Alkyl acrylates	Styrene	Japan 33,581	1976	DuPont
Molding resins	Isobutylene	Ethyl acrylate	Britain 1,476,765	1977	Exxon Research
Molding resin	Styrene	Indene	United States 4,082,820	1978	Standard Oil
Laminating and molding resins	Styrene	Indene	United States 4,117,218	1978	Standard Oil
Rubber modifier molding resins	Styrene	Methacrylonitrile	W. Germany 2,653,146	1978	Bayer A.G.
Thermoplastic moldings	Styrene	$\alpha$ -Olefins	United States 4,137,281	1979	Standard Oil
Heat-stable molding com-positions	Acrylonitrile	Styrene	United States 4,167,543	1979	Bayer A.G.
Impact resistant	Styrene	$\beta$ -Pinene	United States 4,172,861	1979	Standard Oil
High impact moldings	Styrene	Indene	Britain 1,558,052	1979	Standard Oil
Heat-resistant moldings	Styrene	Acrylonitrile	Japan 28,355	1979	Asahi Dow
Polyolefin laminates	Ethylene	Vinyl acetate	Japan 101,883	1979	Nippon Petrochemicals
Molded optical parts	Vinyl acetate	Diallyl esters	Japan 110,289	1979	Ito Kagaku Kogyo
High heat distortion ther-moplastics	Styrene	Acrylonitrile	United States 4,197,263	1980	Standard Oil
Moldable rubber blends	Butadiene	Styrene	United States 4,221,880	1980	ARCO Polymers
Moldable rubber blends	Styrene	Acrylonitrile	United States 4,223,096	1980	Monsanto
Molding resins	Acrylonitrile	Styrene	Britain 1,578,380(384)	1980	Bayer A.G.
Improved rubber moldings	Acrylonitrile	Styrene	Europe 9,529	1980	Monsanto
Glass-fiber reinforced castings	Styrene	Methyl methacrylate	W. Germany 2,934,352	1980	Sumitomo Chemical
Impact-resistant molding blends	Acrylonitrile	Styrene	Japan 21,460	1980	Toray Industries
	Methyl methacrylate	Styrene			
Transparent, heat-resis-tant molding resin	Styrene	Methyl methacrylate	Japan 102,614	1980	Asahi Dow
Optical parts	Allyl acetates	Vinyl acetate	Japan 3,529	1981	Ito Kogaku



Heat resistant molding resins	Styrene	Acrylonitrile	Japan 41,214 (215)	1981	Mitsubishi Monsanto
Heat stable moldings	Styrene	Acrylonitrile	Europe 1,625	1981	Bayer A.-G.

POLYMER ADDITIVES

Wax compositions	Alkyl acrylates	Alkyl methacrylates	Britain 993,794	1965	.Rohm & Haas
Polyolefins modifiers	Styrene	Divinyl benzene	Britain 1,132,645	1968	Tokuyama Soda
Polyolefin stabilizers	Styrene	Dinvyl benzene	Japan 26,859(60)	1971	Tokuyama Soda
Polypropylene foam additive	Monoethyl maleate	Styrene	Japan 24,499	1973	Tokuyama Soda
Modified polyethylenes	Ethylene	Vinyl acetate	E. Germany 107,059	1974	G. Gladigau, et al.
PVC modifiers	Vinyl acetate	Vinyl chloride	Japan 9,105	1974	Kuraray Plastics
PVC modifier	Vinyl acetate	Vinyl chloride	Japan 25,543	1979	Kansai Paint

POLYMER ALLOYS

Polymer alloys—moldings	Ethylene	Vinyl acetate	W. Germany 2,340,743	1974	VEB Leuna-Werke
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PRINTING INKS

Ink resins	Vinylidene chloride	Acrylonitrile	Netherlands 12,362	1966	Kureha Chemical
Ink resins	Vinylidene chloride	Vinyl chloride	United States 3,300,435	1967	Kureha Chemical
Ink resins	Vinyl chloride	Vinylidene chloride	Britain 1,064,045	1967	Kureha Chemical
Printing paste thickener	Butyl vinyl ether	Vinyl propionate	France 2,009,475	1970	Badische Anilin
Ink resins	Vinyl chloride	Vinyl acetate	Belgium 826,004	1975	—
Water-soluble inks	Styrene	Methyl methacrylate	Japan 65,311	1975	Sumitomo Chemical
Transparent, printable coatings	Vinyl acetate	Vinyl chloride	Japan 92,811	1979	—

PROTEIN FIXING AGENTS

Soluble protein fixing agent	Acrylamide	N,N'-Bismethylene-bisacrylamide	W. Germany 1,908,290	1970	Boehringer Mannheim A.G.
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Table A.1 (cont.)

Applications	Monomer M <sub>2</sub>	Monomer M <sub>3</sub>	Patent	Year	Assignee
SEALANTS/CAULKS					
Air curable Sealing compositions	Butyl acrylate	Vinyl triethoxysilane	United States 3,423,376	1969	Thiokol Chemical
	Isoprene	Styrene	Japan 135,846	1979	Shiraishi Kogyo
VINYL PLASTISOLS					
Plastisols	Vinyl chloride	Vinyl acetate	Japan 13,015	1967	Electro Chemical Industry
Plastisol compositions	Vinyl acetate	Vinyl chloride	Japan 52,161	1975	Kansai Paint
WATER-SOLUBLE POLYMERS					
Clay beneficiation agent— well drilling additive	Ethylene	Diallyl ether	United States 3,070,544	1962	Monsanto
Flocculants for water clarification	Acrylamide	Methacrylic acid	United States 3,256,141	1966	Nalco Chemical
Aqueous thickening addi- tives	Alkyl vinyl ethers	Divinyl benzene	United States 3,530,102	1970	Union Carbide
Aqueous thickening agent	1-Octadecene	Methyl vinyl ether	South Africa 4,466	1970	Imperial Chemical
Aqueous thickening agents	Styrene	Alkyl vinyl ethers	United States 3,723,375	1973	GAF
Water-soluble	1-Hexene	Styrene	W. Germany 2,413,922	1974	Toray Industries, Inc.
Thickening agents	Acrylic acid	Diallyl ether	Japan 130,485	1974	Wako Pure Chemical
Aqueous thickening agent	Indene	Divinyl benzene	United States 4,090,998	1978	Standard Oil
Water-soluble resins	Acrylamide	Acrylic acid	Britain 1,523,408	1978	Cassella Farbenwerke
Thickening agents for aqueous latices systems	Vinyl benzyl ethers	Styrene	United States 4,105,649	1979	Dow Chemical
Water-soluble lacquers	Butyl acrylate	Methyl methacrylate	Austria 350,685	1979	Vianova Kunstharz
Thermal reversible aqueous gels	Vinyl acetate	Maleimide	Japan 30,244	1979	Konishi



Table A.2. Maleic Anhydride–Styrene Copolymer Patents

Modifications/Applications	Patent	Year	Assignee
<i>PRODUCTION PROCEDURE</i>			
Preparation procedure	United States 2,286,062	1942	DuPont
Production procedure	United States 2,297,351	1942	DuPont
Photopolymerization procedures	United States 2,297,301	1943	PPG
Production procedures and coatings	United States 2,333,512	1943	Westinghouse
Production procedures	United States 2,345,013	1944	Socony-Vacuum Oil
Production procedures	United States 2,370,943	1944	DuPont
Production procedures	United States 2,375,256	1945	U.G.I.
Production procedures	United States 2,375,960	1945	Union Carbide
Production procedures	Canada 423,245	1944	Canadian Industries
Production procedures	United States 2,403,962	1946	L. Auer
Preparation procedure	United States 2,424,814	1947	PPG
Preparation procedure	United States 2,430,313	1947	DuPont
Production procedures	Canada 442,235	1947	Canadian Kodak
Production procedures and coatings	United States 2,454,284	1948	DuPont
Preparation procedure	United States 2,490,489	1949	DuPont
Production procedures	United States 2,514,389	1950	Monsanto
$\beta$ -Nitrostyrene retarder for copolymer preparation	United States 2,537,015	1951	Monsanto
Preparation procedures	United States 2,537,020	1951	Monsanto
Preparation procedure	Britain 650,838	1951	Monsanto
Production procedures	United States 2,047,398	1952	GAF
Preparation procedure	United States 2,606,891	1952	Rohm & Haas
Production procedures	United States 2,675,310	1954	Monsanto
Production procedures	United States 2,838,475	1958	Monsanto
Half-ester preparation	W. Germany 1,046,884	1958	Dynamit AKT
Production procedures	Italy 601,425	1960	Montecantini
Preparation procedure	United States 3,085,994	1963	Sinclair Research
Purification of copolymer	W. Germany 1,159,649	1963	Bergwerksverband G.m.b.H.
Purification of resins	France 1,357,288	1964	Bergwerksverband G.m.b.H.
Production procedures	France 1,360,001	1964	Badische Anilin
Amide production procedure	W. Germany 1,179,001	1964	Farbriken Bayer A.G.
Production procedures	United States 3,178,395	1965	Sinclair Research
Production procedures	Britain 980,113	1965	Sinclair Research
Production procedures	France 84,269	1965	Sinclair Research
Production procedures	Netherlands 6,790	1965	Farbwerke Hoechst
Production procedures	Britain 1,026,145	1966	Monsanto
Ester derivative production procedures	United States 3,342,782	1967	Sinclair Research
Copolymer production procedures	United States 3,342,787	1967	Sinclair Research

Table A.2 (cont.)

Modifications/Applications	Patent	Year	Assignee
Copolymer production procedures	United States 3,392,155	1968	Sinclair Research
Production procedures—homogeneous polymer	United States 3,401,153	1968	Dow Chemical
Copolymer production procedure	United States 3,404,135	1968	Rheinpruessen A.G.
Copolymer production procedures	United States 3,418,292	1968	Sinclair Research
Copolymer production procedure	Czechoslovakia 126, 961	1968	J. Zdrazil
Copolymer production procedure	France 1,511,921	1968	Monsanto
Production procedures	United States 3,423,355	1969	Sinclair Research
Production procedures	United States 3,423,373	1969	Sinclair Research
Production procedure—chlorostyrene copolymer	United States 3,440,229	1969	Dow Chemical
Production procedures	United States 3,451,979	1969	Sinclair Research
Production procedures	France 1,552,589	1969	Farbwerke Hoechst
Decarboxylated copolymer	W. Germany 1,902,735	1970	Rheinpreussen A.G.
Production procedure	W. Germany 2,149,584	1972	Allied Chemical
Copolymer production procedure	United States 3,725,360	1973	Dow Chemical
Imide derivatives—production procedures	W. Germany 1,570,594	1973	Bayer A.G.
Copolymer production procedures	Japan 43,664	1973	Research Institute for Product Development
Continuous production procedures	W. Germany 2,343,871	1975	BASF A.G.
Production procedure—high molecular weight polymer	E. Germany 128,163	1977	VEB Leuna-Werke
Production procedures for resins	Czechoslovakia 7,629	1978	Romanov A
Ester derivatives—production procedures	Japan 20,554	1978	Hitachi Chemical
Suspension polymerization procedures	United States 4,145,375	1979	U.S. Steel Corp.
Production procedure—alkali metal bifuoride catalysts	Britain 1,556,319	1979	Allied Chemical
Powdered polymer production procedures	W. Germany 2,828,630	1979	Hitachi Chemical
Production procedure	United States 4,180,637	1980	Dow Chemical
Coalgomers production procedures	U.S.S.R. 73,709	1980	Central Scientific Research and Design Institute
Continuous bulk method	Europe 27,274	1981	Daicel Chemical
Improved production procedure	Japan 30,416	1981	Sumitomo Chemical



Table A.2 (cont.)

Modifications/Applications	Patent	Year	Assignee
Solution production procedure	U.S.S.R. 755,801	1981	Kalinin University
<i>ADHESIVES</i>			
Adhesives and coatings	United States 2,392,139	1946	PPG
Rewettable gum tape	United States 2,624,715	1953	Monsanto
Adhesive derivatives	United States 2,667,462	1954	Monsanto
Salts in surgical adhesives	United States 3,005,802	1958	Johnson & Johnson
Esters in pressure-sensitive adhesives	Britain 798,806	1958	Johnson & Johnson
Esters as pressure-sensitive adhesives	United States 2,870,128	1959	Johnson & Johnson
Modifier for epoxy resins	W. Germany 1,100,113	1961	Westinghouse Electric
Epoxy resin modifier	United States 3,099,638	1963	Westinghouse Electric
Preparation—use as coatings, adhesives	France 1,322,807	1963	Texas Butadiene Chemical
Crosslinked resins	France 1,452,657	1966	Monsanto
Amide derivatives as adhesion promoters	Netherlands 4,989	1966	Balm Paints
Rubber adhesive modifier	France 1,476,225	1967	Courtaulds, Ltd.
Epoxy thermosetting resin blends	United States 3,417,045	1968	Dow Chemical
Epoxy thermosetting resin blends	United States 3,417,162	1968	Dow Chemical
Epoxy curing agent-modifier	Czechoslovakia 126,116	1968	I. Wiesner
Epoxy crosslinker and modifier	United States 3,422,076	1969	American Cyanamid
Paper—adhesives	France 1,583,641	1969	Farbenfabriken Bayer
Adhesive compositions	W. Germany 1,915,508	1969	Dow Chemical
Thermosetting materials	United States 3,538,080	1970	Dow Chemical
PVA emulsifier for wood adhesives	Japan 6,438	1970	Arakwa Forest Chemical Ind.
Flexible polymer formulations—sheet bonding	Czechoslovakia 146,692	1972	E. Mueck
Imide copolymers for nonflammable foams	France 2,100,996	1972	Dow Chemical
Adhesives resins	France 2,103,060	1972	Lubrizol Corp.
Plywood adhesive	Japan 27,242	1972	Kuraray Co.
Multifilm layer adhesives—packaging films	W. Germany 2,041,373	1972	Badsche Anilin
Epoxy resin crosslinker	W. Germany 2,149,583	1972	Allied Chemical
Carbon fiber resin adhesion promoter additive	W. Germany 2,212,789	1972	Atomic Energy Commission
Epoxy resin crosslinker	W. Germany 2,118,690	1973	Reichhold-Albert-Chemie
Plywood adhesive formulations	Japan 91,136	1973	Kuraray Co.

Table A.2 (cont.)

Modifications/Applications	Patent	Year	Assignee
Ammoniated derivatives for label adhesives	United States 3,857,803	1974	Borden Ind.
Epoxy resin modifiers and hardeners	Czechoslovakia 154,379	1974	P. Jarolimek
Wood and paper adhesives	Japan 8,534	1974	Kuraray Co.
Plywood adhesive resins	Japan 8,535	1974	Kuraray Co.
Plywood adhesive formulations	Japan 8,537	1974	Kuraray Co.
Flexible electric circuit adhesives	Japan 22,439	1974	Sumitomo Bakelite
Wood-fiber blends for wood adhesives	United States 3,894,975	1975	Champion International Corp.
Epoxy hardener for flexible printed circuits	W. Germany 2,363,259	1975	Sumitomo Bakelite
$\alpha$ -Methylstyrene copolymer for epoxy curing	W. Germany 2,410,728	1975	Sumitomo Bakelite
Aqueous plywood adhesive formulations	Japan 100,122	1975	Nippon Oils & Fats Co.
Epoxy resin hardener for composites	Japan 153,098	1975	Sumitomo Bakelite
Epoxy resin hardeners	U.S.S.R. 448,742	1975	Institute of Petro-Chemical Process
Metal-polymer adhesives	W. Germany 1,934,434	1978	Mitsubishi
Metal-polyolefin adhesives	Japan 19,629	1978	Mitsubishi
Amides as epoxy resin modifier	Japan 90,397	1978	Kansai Paint
Polyester adhesive compositions	Japan 33,253	1979	Toyo Spinning
Dental resin cements	Japan 47,387	1979	Sankin Ind.
Polyester film adhesive	United States 4,202,923	1980	Hoechst A.G.
NH <sub>3</sub> Derivatives—adhesives for corrugated boards	Japan 63,250	1980	Kindai Chemical Ind.
Ester derivatives—adhesive for corrugated boards	Japan 69,440	1980	Kindai Chemical Ind.
Component for hot melt metal adhesives	Japan 84,301	1980	Mitsubishi Chemical
Hot-melt wood adhesives	Romania 65,786	1980	M. Banta

*BOILER SCALE CONTROL AGENT*

Acids as boiler scale removal	United States 2,723,956	1955	National Aluminate Corp.
Salt derivatives—boiler scale removal agents	South Africa 2,227	1968	Nalco Chemical
Acid and salt derivatives as boiler scale inhibitors	United States 3,650,970	1972	Atlantic Richfield



Table A.2 (cont.)

Modifications/Applications	Patent	Year	Assignee
Boiler scale removal agent	United States 3,755,264	1973	Amicon Corp.
Water treatment resins	W. Germany 2,405,192	1974	Ciba-Geigy
CELLULAR MATERIALS			
Foamed plastics	Britain 1,140,146	1969	Imperial Chemical
Nucleating agent—poly-styrene foam	South Africa 5,187	1969	Dow Chemical
Insulating materials—foams	United States 3,492,196	1970	Dow Chemical
Amide derivative foams	United States 3,537,885	1970	Dow Chemical
Cellular plastic products	United States 3,547,838	1970	Dow Chemical
Cellular products	South Africa 2,238	1970	Imperial Chemical
Imide derivatives in structural foams	France 2,068,044	1971	Dow Chemical
Amide for foam-cement combinations	Japan 16,519	1971	Omi Kenshi Spinning Co.
Structural foam resins	United States 3,637,459	1972	Dow Chemical
Plastic foams for roof insulation	United States 3,672,951	1972	Dow Chemical
Structural foams	France 2,096,809	1972	Dow Chemical
Component resins for foams	W. Germany 2,101,282	1972	Farbwerke Hoechst
Esters in press molding foams	W. Germany 2,218,958	1972	Sinclair Koppers
Cellular product resins	Britain 1,316,823	1973	Dow Chemical
Halogenated alcohol modified for foams	United States 4,059,545	1977	Dow Chemical
Cellular polystyrene with reduced flammability	Belgium 861,028	1978	ARCO Polymers
Foamed copolymer products	Britain 1,546,300	1979	Dow Chemical
Fire resistant nondrip foams	France 2,406,644	1979	Dow Chemical
Foamable polymeric alloy compositions	United States 4,207,402	1980	Monsanto
PPO modifier—foams	Britain 1,577,459	1980	General Electric
Foam materials	Japan 135,127	1980	Sekisui Chemical
COATINGS			
Preparation procedure	United States 2,286,062	1942	DuPont
Production procedure	United States 2,297,351	1942	DuPont
Water soluble	Britain 549,682	1942	DuPont
Moldings and coatings	United States 2,320,724	1943	PPG
Production procedures and coatings	United States 2,333,512	1943	Westinghouse
Production procedures	United States 2,375,960	1945	Union Carbide
Plasticizers	United States 2,384,085	1945	PPG

Table A.2 (cont.)

Modifications/Applications	Patent	Year	Assignee
Color photography resins	Britain 569,646	1945	DuPont
Adhesives and coatings	United States 2,392,139	1946	PPG
Halogenated materials in electrical insulation	United States 2,406,319	1946	Sprague Electric Co.
Plasticized resins	United States 2,407,413	1946	PPG
Preparation procedure	United States 2,424,814	1947	PPG
Preparation procedure	United States 2,430,313	1947	DuPont
Production procedures and coatings	United States 2,454,284	1948	DuPont
Coatings	Britain 599,277	1948	Union Carbide
Esters in thermosetting materials	United States 2,479,486	1949	PPG
General purpose	United States 2,505,844	1950	U.S. Rubber
Coatings and laminates	United States 2,516,309	1950	Monsanto
Modified resins in surface coatings	United States 2,543,601	1951	Rohm & Haas
Crosslinked resins in surface coatings	United States 2,543,602	1951	Rohm & Haas
Crosslinked resins	United States 2,554,959	1951	Rohm & Haas
Hydrolysis of resins	United States 2,565,147	1951	Quaker Chemical
Perfluoresters	United States 2,508,504	1952	Purdue Research Foundation
Crosslinked resins	United States 2,591,587	1952	Monsanto
Ester derivatives as protective coatings	United States 2,640,819	1953	Monsanto
Crosslinked salt resins as protective coatings	United States 2,647,886	1953	Monsanto
Cellulose moisture proofing agents	United States 2,650,172	1953	American Viscose
Cellulose moisture proofing agents	United States 2,650,177	1953	American Viscose
Ester derivatives	Dutch 72,404	1953	Adriaan Honig's Kunsthars Ind.
Hydantoin derivatives in light-sensitive resins	United States 2,719,141	1955	Eastman Kodak
Esters with drying oils	Britain 723,115	1955	Adriaan Honig's Kunsthars Ind. N.V.
Paint binder	W. Germany 927,461	1955	Farbwerke Hoechst
Electrolytically conductive resins	United States 2,730,768	1956	Ionics, Inc.
Crosslinked resins in electroconductive materials	United States 2,731,408	1956	Ionics, Inc.
Crosslinked resins in electroconductive materials	United States 2,731,411	1956	Ionics, Inc.
Modified resins as photo-active materials	United States 2,751,373	1956	Eastman Kodak
Ester salts in coatings	United States 2,757,153	1956	Monsanto



Table A.2 (cont.)

Modifications/Applications	Patent	Year	Assignee
Modified resins as photo-curable materials	United States 2,811,509	1957	Eastman Kodak
Chalcone derivatives for photo-resists	United States 2,816,091	1957	Eastman Kodak
Water-soluble materials	W. Germany 1,016,936	1957	Dynamit AKT
Derivatives in photoactive films	United States 2,824,084	1958	Eastman Kodak
Photoactive films	United States 2,835,656	1958	Eastman Kodak
Preparative procedure for granular polymer	W. Germany 968,130	1958	Dynamit AKT
Epoxy resin curing agents	W. Germany 1,033,047	1958	Badische Anilin
Half-ester preparation	W. Germany 1,046,884	1958	Dynamit AKT
Cable insulating materials	Japan 295	1958	Nippon Telegraph and Telephone
Enteric coating resins	United States 2,897,121	1959	Upjohn
Salts as antistatic coatings for plastics	United States 2,912,413	1959	Monsanto
Ester derivative in alkyds	Britain 819,746	1959	Bakelite Ltd.
Derivatives in photoactive systems	Britain 822,861	1959	Farbenfabriken Bayer AKT
Protective coatings for drugs	W. Germany 1,063,758	1959	Upjohn
Esters in metal primers	U.S.S.R. 133,545	1960	A.A. Blagonravova
Salts for cellulosics	United States 3,034,928	1962	DuPont
Imide derivatives in photographic films and detergent additives	United States 3,048,487	1962	Eastman Kodak
Derivatives in photoactive materials	United States 3,050,387	1962	Azoplate Corp.
Preparation procedure	United States 3,085,994	1963	Sinclear Research
Epoxy resin modifier	United States 3,099,638	1963	Westinghouse Electric
Electrophotographic coatings	Britain 944,277	1963	Kalle A.G.
Preparations for coatings and adhesives	France 1,322,807	1963	Texas Butadiene Chemical
Epoxy curing agent	United States 3,118,848	1964	Cook Paint & Varnish
Medicinal tablet coatings	United States 3,132,075	1964	Upjohn
Ester derivatives in cellulose coatings	United States 3,149,020	1964	Fom-Cor Corp.
Ester derivatives as epoxy resin curatives	Britain 963,942	1964	Dow Chemical
Ester derivatives as epoxy resin curatives	Britain 963,944	1964	Dow Chemical
Coating, molding, casting and laminating resin blends	United States 3,225,115	1965	Union Carbide
Derivatives in coating systems	Belgium 659,264	1965	Dow Chemical
Stove varnish resins	Belgium 662,973	1965	Bergwerksverband G.m.b.H.

Table A.2 (cont.)

Modifications/Applications	Patent	Year	Assignee
Colored lacquer resins	Belgium 669,479	1965	Badische Anilin
Electrophotographic films	Britain 1,004,461	1965	Gevaert Photo Producten N.V.
Medicinal tablet coatings	Britain 1,005,424	1965	Abbott Laboratories
Aqueous baking lacquers for tin plate	Netherlands 4,491	1965	Bergwerksverband G.m.b.H.
Photographic film antihala- tion layer	U.S.S.R. 173,602	1965	G.N. Lapshin
Alkali-soluble floor polishes	United States 3,234,158	1966	Borden
Waterborne coatings	United States 3,245,933	1966	Sinclair Research
Ester derivatives for water- based coatings	United States 3,256,233	1966	Monsanto
Photoconductive resins	United States 3,261,709	1966	Arthur D. Little
Propoxylated resin for thermosetting coatings	United States 3,262,897	1966	Catalin Corp.
Phosphorus ester deriva- tives—fire-retardant coatings	United States 3,262,918	1966	Armstrong Cork
Radiation-curable materials	United States 3,281,263	1966	Dow Chemical
Enteric tablet coatings	United States 3,282,790	1966	Upjohn
Crosslinked resins	France 1,452,657	1966	Monsanto
Crosslinked phosphorus resins	United States 3,303,042	1967	Westinghouse Electric
Crosslinked resins in elec- trolytic processes	United States 3,305,463	1967	PPG
Thermosetting epoxy blends	United States 3,317,457	1967	Dow Chemical
Epoxy blends for metal coatings	United States 3,321,424	1967	Swift & Co.
Allyl esters in thermosetting resins	United States 3,326,864	1967	Dow Chemical
Metal coatings	United States 3,331,886	1967	Dow Chemical
Polyol derivative for decora- tive coatings, moldings, and laminates	United States 3,336,259	1967	Dow Chemical
Thermosetting resins	United States 3,357,936	1967	Dow Chemical
Microencapsulation resin for emulsion systems	W. Germany 1,248,016	1967	National Cash Register
Thermosetting waterborne coatings	Netherlands 10,969	1967	National Starch & Chemical Corp.
Half amide-ester pigment binders	United States 3,368,987	1968	Monsanto
Thermosetting wire coatings, paper impregnants	United States 3,381,054	1968	Monsanto
Thermosetting materials	United States 3,381,055	1968	Monsanto
Diol blends for thermo- setting materials	United States 3,408,337	1968	Dow Chemical
Epoxy thermosetting resin blends	United States 3,417,045	1968	Dow Chemical
Epoxy thermosetting resin blends	United States 3,417,162	1968	Dow Chemical



Table A.2 (cont.)

Modifications/Applications	Patent	Year	Assignee
Photographic films	France 1,513,823	1968	Fuji Photo Film
Epoxy blends for thermo-setting materials	France 1,531,763	1968	Dow Chemical
Air-drying water-based paint resins	W. Germany 1,273,100	1968	Rheinpruessen A.G.
Solvent-resistant appliance coatings	South Africa 6,069	1968	Balm Paints
Epoxy crosslinker and modifier	United States 3,422,076	1969	American Cyanamid
Allyl ester themosetting resins	United States 3,429,946	1969	Sinclair Research
Explosives coatings binder	United States 3,444,728	1969	American Cyanamid
Thermosetting materials	Britain 1,141,859	1969	Dow Chemical
Photoactive resins for image formation	France 1,555,957	1969	GAF Corp.
Allyl esters—air-dry varnishes	France 1,577,476	1969	Cassella Farbwerke Manikur
Electrophoretic systems	France 2,015,964	1969	Chemische Werke
Aqueous baking lacquers	W. Germany 1,289,934	1969	Bergerksverband G.m.b.H.
Ester derivatives—pigment binder resins	W. Germany 1,814,569	1969	Titangesellschaft G.m.b.H.
Floor polish formulations	W. Germany 1,915,960	1969	Unilever N.V.
Thermosetting resins	Japan 25,894	1969	Japan Catalytic Chemical Ind.
Allyl ester derivatives—thermosetting resins	Japan 26,112	1969	Riken Synthetic Resin Co.
Protective colloid resins	Poland 58,126	1969	Z. Debowski
Lithographic plate resins	South Africa 8,967	1969	Algraphy Ltd.
Heat-resistant materials	U.S.S.R. 235,996	1969	Y. A. Yakubovich
Imides for thermosetting materials	United States 3,494,979	1970	Sinclair Research
Emulsifiers for latex polymers amide-salt derivatives for diesel fuel additives	United States 3,505,156	1970	Imperial Chemical
Hydroximide derivatives	United States 3,520,852	1970	Sinclair Research
Thermosetting decorative materials	United States 3,528,935	1970	Sinclair Research
Thermosetting decorative materials	United States 3,528,939	1970	Sinclair Research
Thermosetting materials	United States 3,529,993	1970	Pacific Vegetable Oil Corp.
Thermosetting materials	United States 3,538,080	1970	Dow Chemical
Rapid-dry varnish binder	Czechoslovakia 137,406	1970	K. Klatil
Varnish and paint resins	France 1,601,132	1970	Chemische Werke
Cinnamyl ester derivatives as photoactive films	France 2,009,112	1970	GAF Corp.
Transparent, acid-resistant materials	France 2,010,152	1970	Scholven-Chemie A.G.

Table A.2 (cont.)

Modifications/Applications	Patent	Year	Assignee
Waterborne resins	France 2,015,280	1970	Sybron Corp.
Polyester photographic film subbing layer	France 2,221,750	1970	Fuji Photo Film
Insulating foams and wire coatings	W. Germany 1,811,166	1970	Farbenfabriken
Photographic film antistat	W. Germany 1,815,944	1970	Agfa-Gevaert A.G.
Modifier reactant for malamine-formaldehyde resins	W. Germany 1,910,472	1970	Farbwerke Hoechst
Heat-hardenable resins	W. Germany 2,915,576	1970	Badische Anilin
Encapsulation resins	W. Germany 1,917,738	1970	Farbenfabriken Bayer
Electrophoretic emulsion lacquering baths	W. Germany 1,198,630	1970	Reichhold-Albert Chemie
Ester derivatives in thermosets	W. Germany 1,919,722	1970	Sinclair Koppers
Protective resins for wood	W. Germany 1,922,942	1970	Th. Goldschmidt A.G.
Thermosetting resins	W. Germany 1,923,922	1970	Reichhold-Albert-Chemie
Mercaptan derivatives for thermosets	W. Germany 1,930,217	1970	Farbenfabriken
Photoactive derivatives	W. Germany 1,955,271	1970	Kansai Paint Co.
Photographic antihalation agents	W. Germany 2,021,306	1970	3M Co.
Fluorescent lamp coating suspending agent	Japan 7,421	1970	Tokyo Shibaura Electric Co.
Amide derivatives for thermosets	Japan 11,152	1970	K. Shinohara
Photosensitive resin compositions	Japan 34,705	1970	Konishiroku Photo. Ind.
Crosslinked resins for coatings	U.S.S.R. 202,520	1970	Institute of Chemistry and Physics
Metal coatings for deforming operations	United States 3,568,486	1971	Montgomery Co.
Imide derivatives for thermosets	United States 3,578,641	1971	Monsanto
Photoconductive binders	United States 3,615,419	1971	National Starch
Acid copolymer for thermosetting resins	United States 3,629,357	1971	DeSoto, Inc.
Lithographic printing plate resins	Britain 1,243,963	1971	Howson-Algraphy
Electrophotographic film resins	Britain 1,244,944	1971	Ilford, Ltd.
Dispersants for emulsion polymers	Britain 1,244,949	1971	Ilford, Ltd.
Photosensitive printing plate resins	Britain 1,357,168	1971	Badische Anilin
Photosensitive printing plate resins	France 2,111,159	1971	Badische Anilin



Table A.2 (cont.)

Modifications/Applications	Patent	Year	Assignee
Crosslinked imides	W. Germany 1,956,285	1971	Badische Anilin
Metal coatings resins	W. Germany 2,004,062	1971	Montgomery Co.
Antistatic coatings for photo-graphic films	W. Germany 2,011,649	1971	Agfa–Gevaert
Fire-resistant, thermosetting resins	W. Germany 2,018,193	1971	Farbenfabriken Bayer
Photopolymerizable copying resin	W. Germany 2,027,467	1971	Kalle A.G.
Photoactive coatings for photographic film	W. Germany 2,044,449	1971	Fuji Photo Film
Photopolymerizable copying resin	W. Germany 2,060,576	1971	Kalle A.G.
Water-repellent finishes for films and fibers	Japan 6,556	1971	Omi Kenshi Spinning Co.
Antistatic coatings for photographic films	United States 3,634,336	1972	Eastman Kodak
Melamine–formaldehyde resin modifier	United States 3,646,044	1972	DeSoto, Inc.
K salt and rubber coatings	United States 3,669,718	1972	Dow Chemical
Decarboxylated resin	United States 3,682,868	1972	Rheinpreussen
Acid polymer dehydration	United States 3,687,906	1972	Dow Chemical
Hair waving formulations	United States 3,693,633	1972	Oreal S.A.
Decarboxylated resins	Britain 1,298,153	1972	Deutsche Texaco
Imide copolymers for nonflammable foams	France 2,100,996	1972	Dow Chemical
Thermosetting resins	Japan 94,772	1972	Matsushita Electric Works
Photographic film antistatic resins	W. Germany 2,036,717	1972	Agfa–Gevaert
Grafted and crosslinked copolymers	W. Germany 2,114,372	1972	Badische Anilin
Epoxy resin crosslinker	W. Germany 2,146,439	1972	Atlantic Richfield
Epoxy resin crosslinker	W. Germany 2,149,583	1972	Allied Chemical
Light-sensitive photographic film barrier layer	W. Germany 2,162,277	1972	Polaroid Corp.
Multilayer photographic films modifier	United States 3,723,127	1973	Mitsubishi Paper Mills
Hydroxyl alkyl esters for thermosetting metal coatings	United States 3,741,943	1973	DeSoto, Inc.
Salt derivatives for plastics antistatic coatings	United States 3,753,716	1973	Konishiroki Photo Ind.
Unsaturated derivatives for photoactive curable resins	United States 3,773,545	1973	Badische Anilin
Vinyl unsaturated derivatives for radiation-curable resins	United States 3,773,547	1973	Badische Anilin
Thickener for latex polymers	United States 3,779,970	1973	Dow Chemical

Table A.2 (cont.)

Modifications/Applications	Patent	Year	Assignee
Photographic film subbing layer resins	Britain 1,303,363	1973	Fuji Photo Film
Photoconductive resins for electron beam recording	Britain 1,421,026	1973	Hoechst AKT
Photoconductive resins for electron beam recordings	France 2,173,237	1973	Kalle A.G.
Epoxy resin crosslinker	W. Germany 2,118,690	1973	Reichhold-Albert-Chemie
Photosensitive copying paper resins	W. Germany 2,147,947	1973	Kalle A.G.
Dye-sensitive photographic resins	W. Germany 2,160,812	1973	Kalle A.G.
Ester derivatives for stoving lacquers	W. Germany 2,165,491	1973	Deutsche Texaco
Mordants for photographic materials	W. Germany 2,236,089	1973	VEB Filmfabrik Co.
Electrostatic paper coating resins	W. Germany 2,237,008	1973	Ricoh Co.
Acid copolymer for electrophotographic color development	W. Germany 2,248,191	1973	Canon KK
Electrophotographic imaging agent resin component	W. Germany 2,256,021	1973	Canon KK
Unsaturated derivatives for radiation-curable resins	W. Germany 2,306,531	1973	3M Co.
Glass bottle coating formulations	W. Germany 2,309,777	1973	Dart Industries
Ester salt derivatives for plastic coatings	W. Germany 2,310,469	1973	Konishiroku Photo Ind.
Thermosetting resins	W. Germany 2,318,555	1973	Atlantic Richfield
Photographic film resins	W. Germany 2,328,240	1973	Konishiroku Photo Ind.
Allyl esters for electron-beam-curable resins	Japan 92,025	1973	Toray Industries, Inc.
Amide derivatives as electrophotographic resins	United States 3,783,019	1974	Kohjin Co.
Water-based binders for magnetic tape	United States 3,795,539	1974	ADM Tronics
Unsaturated esters for radiation-curable resins	United States 3,825,430	1974	3M Co.
K salt derivative	United States 3,835,122	1974	U.S. Atomic Energy Comm.
Sulfonated resins for antistatic agents	Britain 1,357,522	1974	Kodak Ltd.
Chrysolite asbestos fiber coatings	Canada 956,849	1974	Canadian Patent and Development Ltd.
Epoxy resin modifiers and hardeners	Czechoslovakia 154,379	1974	P. Jarolimek
Stoving lacquer formulations	W. Germany 2,255,668	1974	Deutsche Texaco



Table A.2 (cont.)

Modifications/Applications	Patent	Year	Assignee
Powder metal binder	W. Germany 2,300,093	1974	BASF A.G.
Light crosslinkable photo-resist resins	W. Germany 2,310,307	1974	Rolle A.G.
Sulfonated resins for poly-ethylene coatings	W. Germany 2,326,759	1974	F. Schoeller
Coatings for photographic films	W. Germany 2,344,785	1974	Fuji Photo Film
Binder resins for coatings	W. Germany 2,345,493	1974	Dow Chemical
Epoxy crosslinker for photographic subbing layers	W. Germany 2,349,494	1974	Fuji Photo Film
Epoxy hardener for dry transfer colorations of metallic surfaces	W. Germany 2,424,949	1974	Sublistatic Holding S.A.
Thermosensitive copying paper resins	Japan 16,506	1974	Mitsubishi Paper Mills
Water-soluble paint resins	Japan 31,557	1974	Dai Nippon Toryo Co.
Photoresist resins	Japan 69,322	1974	Konishiroku Photo Ind.
Diamine crosslinker for corrosion-resistant coatings	Japan 99,630	1974	Chisako Senda
Flexible printed electronic circuit board resins	Japan 109,476	1974	Sumitomo Bakelite
Amide derivatives for dry film negative photoresists	United States 3,873,319	1975	3M Co.
Self-polishing shoe polish resins	United States 3,912,679	1975	Werner and Mertz G.m.b.H.
Epoxy curing resins	United States 3,997,499	1975	Gulf Oil
Electrostatic (powder) coatings	W. Germany 2,351,477	1975	Deutsche Texaco
Diallylamide derivatives for thermosetting resins	W. Germany 2,361,769	1975	W. R. Grace
Photopolymerizable resins	W. Germany 2,420,409	1975	S. Matsumoto
Electrophoretic resins	W. Germany 2,453,366	1975	Atlantic Richfield
Transfer coating resins	W. Germany 2,457,623	1975	Mecanorma Export A.G.
Imide derivatives for heat-resistant circuit boards	W. Germany 2,519,950	1975	Sumitomo Bakelite Co.
Unsaturated derivatives for thermosetting resins	Japan 96,687	1975	Hitachi Chemical Co.
Amine modified copolymer for photoresist resins	United States 3,932,401	1976	3M Co.
Electrophoretic resins	United States 3,957,004	1976	Atlantic Richfield
Epoxy crosslinker for coatings	United States 3,997,499	1976	Gulf Oil
Timing layer coatings for dye diffusion color photography	France 2,290,698	1976	Eastman Kodak
Flame-retardant plastics and coatings	United States 4,032,509	1977	Monsanto

Table A.2 (cont.)

Modifications/Applications	Patent	Year	Assignee
Halogenated copolymers for fire-retardant coatings	United States 4,048,263	1977	Monsanto
Flame-retardant coatings	United States 4,051,311	1977	Monsanto
Radiation-curable photo- graphic films	Britain 1,481,361	1977	S. Matsumoto
Azide derivatives for photoresists, lithographic plates, radiation-curable polymers	Japan 7,365	1977	Upjohn Co.
Water-soluble derivatives for coatings	Japan 47,827	1977	Hitachi Chemical
Photocurable resins	W. Germany 2,420,409	1978	Matsumoto
Salts to reduce photo- graphic film sticking	Japan 21,646	1978	Fuji Photo Film
Photoconductive recording coatings	Japan 69,038	1978	Fujikura Kasei Co.
Radiation curable	Japan 74,533	1978	Nippon Paint
Photographic film subbing layers	United States 4,120,724	1979	Fuji Photo Film
Binder for organic coatings	Europe 1,779	1979	BASF A.G.
Drying toners for electro- static charge images	W. Germany 2,907,633	1979	Canon
Storage stable crosslinkable resins	Japan 43,938	1979	Shikoku Ka Ken Kogyo
Strippable anticorrosive coatings	Japan 85,233	1979	Sumitomo Metal
Corrosion protection coat- ings for steel	U.S.S.R. 332,748	1979	Z. S. Smolyan
Modifier and curative for epoxy resins	U.S.S.R. 659,578	1979	Yaroslavl Polytechnic Inst.
Ammine derivative anti- static coatings	Czechoslovakia 182,742	1980	S. Kudrna
Photocurable resins	Europe 14,673	1980	Ciba-Geigy A.G.
Antistatic film coatings	W. Germany 2,310,469	1980	Konishiroku Photo
Adhesive repellent coatings	W. Germany 2,845,541	1980	Beiersdorf A.G.
Perfluoroepoxy derivatives as hair spray resins	W. Germany 2,951,922	1980	Daikin Kogyo Co.
Photographic film base materials	Japan 15,267	1980	Konishiroku Photo
Photosetting compositions	Japan 33,770	1980	Nippon Oil Seal Inc.
Ag halide photographic film back coatings	Japan 66,139	1980	Mitsubishi Paper Mills
Alkali salt in coatings	United States 4,243,564	1981	R. C. Mavis
Photocurable etching resists	Japan 8,417	1981	Somar Mfg.

*COMPOSITES*

Plastic copolymer-wood composites	W. Germany 1,273,787	1968	Bochumer Chemie Imhausen Co.
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Table A.2 (cont.)

Modifications/Applications	Patent	Year	Assignee
Explosives coatings binder	United States 3,444,728	1969	American Cyanamid
Nitric acid blasting cap binder resins	United States 3,454,438	1969	American Cyanamid
Reinforced composite resin	United States 3,488,319	1970	Monsanto
Additive to reduce furan resin shrinkage	W. Germany 2,020,260	1971	Chemische Werke
Polybutadiene blends for plastics	United States 3,679,748	1972	Dow Chemical
Wood composite modifiers for plastics	United States 3,765,934	1972	Champion Int. Corp.
Carbon fiber composites binder	W. Germany 2,212,788	1972	Atomic Energy Com- mission
Glass fiber coatings for composites	Japan 88,134	1973	Sumitomo Chemical
Modifier for transparent glass fiber reinforced composites	W. Germany 2,229,129	1974	BASF A.G.
Cellulosic composites modifier	United States 3,869,432	1975	Champion Interna- tional Corp.
Cellulosic composites	United States 3,900,685	1975	Champion Interna- tional Corp.
Inorganic salt derivatives for Portland cement slurries	United States 3,923,717	1975	Dow Chemical
Epoxy resin hardener for composites	Japan 153,098	1975	Sumitomo Bakelite
Modifier for thermoplastics molding blends	W. Germany 2,524,787	1976	General Electric
Epoxy resin hardener for glass fiber composites	W. Germany 2,537,195	1976	Gulf Oil Corp.
Inorganic binders	Japan 5,247	1978	Japan Synthetic Rubber
Composites with reduced flammability	United States 4,136,135	1979	Monsanto Co.
Foamable polymeric alloy compositions.	United States 4,207,402	1980	Monsanto
Modifier for pencil core materials	Japan 1,949	1980	Pentel Co.
Modifier for sand composites	Japan 103,252(253)	1980	Sekisui Chemical
Wood composites	U.S.S.R. 733,979	1980	Academy of Sciences
Epoxide mouldings	Europe 25,178	1981	Union Carbide

CONTROLLED RELEASE POLYMERS

Fungicidal derivatives	United States 2,577,041	1951	Industrial Research Institute, University of Chattanooga
Imide derivatives as sodium nitrite carrier	United States 3,291,731	1966	Esso Research

Table A.2 (cont.)

Modifications/Applications	Patent	Year	Assignee
Iron slow release agent for medicinal use	Netherlands 7,961	1966	Teikoku Hormone Mfg.
Capsule coatings	United States 3,341,466	1967	C. Brynko
Sn + Pb derivatives for microbiocides, insecticides, and fungicides	Britain 1,101,929	1968	—
Microcapsule coatings	South Africa 4,516	1968	National Cash Register
Capsule encapsulation materials	South Africa 5,656	1968	National Cash Register
Capsule encapsulation materials	South Africa 5,745	1968	National Cash Register
Pharmaceutical coatings	Netherlands 12,024	1968	N.V. Philips
Polymeric medicines	Japan 4,790	1969	Shionogi & Co.
Insecticide carriers resins	United States 3,511,798	1970	Sinclair Research
Encapsulation resins	W. Germany 1,917,738	1970	Farbenfabriken Bayer
Animal diarrhea treatment agent	South Africa 126	1970	Monsanto
Tobacco desuckering agents	United States 3,556,763	1971	Atlantic Richfield
Thiamine complexes for medical uses	Japan 12,160	1971	Shionogi and Co.
Hydrazine derivatives as insecticides	United States 3,679,640	1972	Dow Chemical
Ester derivatives for tobacco desuckering agents	United States 3,697,250	1972	Atlantic Richfield
Animal diarrhea control agent	Britain 1,260,451	1972	Monsanto
Carrier for biologically active compounds	E. Germany 108,311	1974	R. Berger
Oxidation-reduction carrier resin	United States 4,065,435	1977	Fuji Photo Film
Oleoophilic particle coatings	Japan 15,551	1977	RICOH
Amino dye carrier for hair	W. Germany 1,617,707	1978	Oreal S.A.
Controlled release medicinals	United States 4,153,682	1979	Shell Oil
Microcapsule coatings	Britain 2,006,709	1979	Mitsubishi Paper
Neocarzinostatin derivatives, inhibition cancer cell growth	United States 4,182,752	1980	Kayaku Antibiotics Research Co.
Hydrogel blends for slow release of pesticides	W. Germany 2,949,531	1980	A. Heslinga
Improved microcapsule compositions	Japan 15,660	1980	Konishiroku Photo

*COSMETIC ADDITIVES*

Flocculants-cosmetic builders	United States 3,432,454	1969	Dow Chemical
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Table A.2 (cont.)

Modifications/Applications	Patent	Year	Assignee
<i>DETERGENT ADDITIVES</i>			
Imide derivatives in photographic films and detergent additives	United States 3,048,487	1962	Eastman Kodak
Polymeric detergent builder	United States 3,485,762	1969	Sinclair Research
Salt derivatives as detergent builders	United States 3,676,373	1971	Gulf Research
<i>DISPERSANT/EMULSIFIERS</i>			
Dispersant agents	United States 2,324,740(51)	1943	Carbide & Carbon Chemicals Corp.
Esters for polyolefin dispersants	United States 2,496,989	1950	DuPont
Salts as oil dispersants	United States 2,504,003	1950	DuPont
Salt as dispersant for polystyrene preparation	United States 2,548,318	1951	Monsanto
Salts as emulsifiers	United States 2,621,169	1952	Publicker Industrial
Emulsifiers for polymer latexes	W. Germany 879,315	1953	Farbwerke Hoechst
Emulsifier for PVC preparation	Japan 4,244	1955	Sumitomo Chemical
Polymeric dispersants	United States 2,816,877	1957	Shawinigan Resins
Salt as dispersant for PVC emulsions	E. Germany 13,583	1957	—
Dispersant for PVC preparation	W. Germany 1,011,623	1957	VEB Chemische-Werke
Collodial Cu stabilizer for hydrogenation reactions	W. Germany 1,023,749	1958	Chemische Fabrik Diiren G.m.b.H.
Salt derivative in nonionic detergents	United States 2,876,201	1959	Dan River Mills
Photographic emulsion binder and dispersants	Belgium 573,005	1959	Gevaert Photo
Vinyl polymerization emulsifiers	W. Germany 1,066,356	1959	Dynamit Nobel
Salt as dispersant for PVC preparation	Japan 445	1959	Nippon Carbide
Color photography emulsion stabilizers	W. Germany 1,073,307	1960	Imperial Chemical
Suspending agent for PVC preparation	United States 2,979,487	1961	Monsanto
Dispersant for emulsion polymerizations	Belgium 619,486	1962	Firestone Tire & Rubber
Salts as polybutadiene recovery agent	Britain 899,154	1962	Chemische Werke Huels
Photographic emulsion stabilizer	W. Germany 1,136,110	1962	Gevaert Photo Producten N.V.

Table A.2 (cont.)

Modifications/Applications	Patent	Year	Assignee
Protective colloids for polishes	Belgium 621,179	1963	Sinclair Research
Photographic film stripping additive	Belgium 624,262	1963	GAF Corp.
Amide derivatives in hair waving formulations	Belgium 629,769	1963	Oreal S.A.
Photographic stripping film additives	Britain 960,050	1964	GAF Corp.
Salt derivatives for emulsion polymerizations	Britain 980,763	1965	Institute Synthetic Rubber
Salt stabilizers for emulsion polymerizations	Britain 996,774	1965	Institute Synthetic Rubber
Synthetic resin dispersant agent	France 1,407,957	1965	Reichold Chemie
PVC emulsifier-stabilizer	Netherlands 772	1965	Dynamit-Nobel
Latex coatings dispersant	United States 3,232,903	1966	Rohm & Haas
Paper coating latexes emulsifier	France 1,450,668	1966	Monsanto
Polyolefins dispersant	W. Germany 1,215,371	1966	VEB Chemische Werke
Ag halide photographic solution emulsifier	Netherlands 17,159	1966	Gevaert-Agfa N.V.
Esters for polish emulsifiers	United States 3,313,755	1967	Knowmark, Inc.
Polyelectrolytes for dispersant	United States 3,340,680	1967	Monsanto
Thickening agent, protective colloid, ion-exchange resins	France 1,466,860	1967	Oesterreichische Stickstoffwerke A.G.
Salts as photographic emulsion flocculant	France 1,474,110	1967	VEB Fotochemische Werke
Ag halide emulsion flocculant	E. Germany 56,165	1967	M. Juergens
Photographic emulsion dispersant	W. Germany 1,241,701	1967	VEB Photochemische Werke
Salt derivatives of allyl esters as emulsifiers for acrylic copolymers	United States 3,363,029	1968	Sinclair Research
Emulsifier for polyethylene polishes	United States 3,380,944	1968	Hooker Chemical
Polymeric dispersants	United States 3,415,745	1968	Sinclair Research
Photographic emulsion coagulant	Britain 1,121,188	1968	VEB Fotochemische Werke
Vinyl chloride polymerization emulsifier	France 1,542,089	1968	VEB Chemische Werke
Photographic emulsion coating coagulant	E. Germany 59,686	1968	H. Welzel
Photographic Ag halide coating dispersant	E. Germany 62,514	1968	H. Welzel



Table A.2 (cont.)

Modifications/Applications	Patent	Year	Assignee
Polyelectrolyte protective colloids	E. Germany 62,915	1968	H. Pobloth
Flocculants, cosmetic builders	United States 3,432,454	1969	Dow Chemical
Polymeric dispersants	United States 3,444,151	1969	Sinclair Research
Ammonium salt-emulsion polishes	United States 3,446,783	1969	Hooker Chemical
Emulsifiers for poly-butadiene production	United States 3,476,735	1969	Farbenfabriken Bayer A.G.
Nucleating agent—polystyrene foam	South Africa 5,187	1969	Dow Chemical
Quaternary amide derivatives for photographic films	United States 3,488,706	1970	Eastman Kodak
Water dispersible flocculant for suspended inorganic solids	United States 3,492,225	1970	Nalco Chemical
Ester derivatives for latex emulsion dispersants	E. Germany 77,066	1970	E. Anton
Anion surface active derivatives	W. Germany 1,900,106	1970	Kao Soap Co.
Polymeric dispersants	W. Germany 1,904,233	1970	Farbenfabriken Bayer
Emulsifier for polymer stabilization	W. Germany 1,946,934	1970	Reichhold–Albert–Chemie
Imide–amide derivatives as mineral oil dispersant	United States 3,575,861	1971	Atlantic Richfield
Ag halide dispersant for photographic emulsions	United States 3,615,624	1971	Eastman Kodak
Oven cleaner additive	United States 3,625,854	1971	Sinclair Research
Clay dispersant for pressure-sensitive copying paper	France 2,066,306	1971	Fuji Photo
Ag halide dispersant for photographic film formulations	W. Germany 1,937,364	1971	Agfa–Gevaert
Opacifier for liquid soap	W. Germany 1,955,557	1971	Unilever N.V.
Salts as emulsion stabilizers	W. Germany 2,013,358	1971	Farbenfabriken Bayer
Rug shampoo detergent additive	W. Germany 2,056,556	1971	Atlantic Richfield
Floor detergent modifier	W. Germany 2,121,926	1971	Unilever N.V.
Salt derivatives for soil and spot removal formulations	W. Germany 2,211,623	1971	3M Co.
Modifier for cleaning wax for floors	Netherlands 6,261	1971	Unilever N.V.
Water emulsion polishing paste stabilizer	U.S.S.R. 311, 945	1971	Scientific Design

Table A.2 (cont.)

Modifications/Applications	Patent	Year	Assignee
Esters as dispersant for PVA latex paints	United States 3,639,325	1972	Atlantic Richfield
Water-based metal working lubricants	United States 3,645,897	1972	Atlantic Richfield
Imide derivatives as hydrolic fluid emulsifiers	United States 3,645,903	1972	Atlantic Richfield
Floor polish resins and dispersants	United States 3,647,732	1972	B. G. Gower
Salts as cutting oil emulsifiers	United States 3,650,978	1972	Atlantic Richfield
Emulsifiers for metal working lubricants	United States 3,657,123	1972	Atlantic Richfield
Hair waving resins and formulations	United States 3,693,633	1972	Oreal S.A.
Modifier for cleaning solutions	United States 3,696,043	1972	Dow Chemical
Cleaning agent dispersant	United States 3,700,599	1972	Economics Laboratory
Stabilizer for dishwasher detergents	United States 3,703,470	1972	W. R. Brennan
Opacifier for particle suspensions	Britain 1,270,408	1972	Champion Paper
Washing agent builder	W. Germany 2,056,814	1972	Chemische Werke
Floor polish emulsifier	W. Germany 2,056,864	1972	Farbwerke Hoechst
Liquid washing dispersant and stabilizer	Poland 65,593	1972	Institute of Chemical Research
Cleaning and polishing formulation additives	United States 3,741,914	1973	Procter & Gamble
Quaternary nitrogen derivatives for photographic emulsions	United States 3,758,445	1973	Eastman Kodak
Floor polish emulsion modifier and stabilizer	United States 3,766,113	1973	Sinclair Oil Corp.
Carpet cleaning resin solutions	France 2,148,939	1973	Tapis Center of Research and Technical Studies
Self-shining shoe polish resin dispersant	W. Germany 2,136,951	1973	Werner and Mertz G.m.b.H.
Floor polish formulation additive	W. Germany 2,247,066	1973	American Home Prod.
Resins for photographic developer solutions	United States 3,785,824	1974	3M Co.
Dispersant for aqueous polish formulations	United States 3,786,012	1974	Atlantic Richfield
Dispersant for latex resins	United States 3,799,901	1974	Dow Chemical
Dispersant for cementitious mixtures	United States 3,819,391	1974	Koppers Co.



Table A.2 (cont.)

Modifications/Applications	Patent	Year	Assignee
Amide salts as washing solution builders	Britain 1,361,641	1974	Chemische Werke Huels
Amide derivatives as emulsifiers for coatings	W. Germany 1,595,704	1974	Bayer A.G.
Ion-exchange resins for washing formulations	W. Germany 2,250,972	1974	BASF A.G.
Ester derivatives as emulsifiers	W. Germany 2,312,616	1974	Reichhold-Albert-Chemie
Ester derivatives as emulsifiers	W. Germany 2,326,979	1974	Reichhold-Albert-Chemie
<i>p</i> -Vinylphenol copolymer as detergent additive	Japan 21,403	1974	Maruzen Oil
Salt derivatives as emulsifiers for polystyrene production	Poland 72,906	1974	K. Mitoraj
Emulsifier for metal working emulsions	U.S.S.R. 433,201	1974	Odessa State University
Self-polishing shoe polish resins	United States 3,912,679	1975	Werner and Hertz G.m.b.H.
Glass surface cleaning solution additives	Canada 968,249	1975	Dow Chemical
Latex emulsifier resins	France 2,252,358	1975	Dow Chemical
Amide derivatives for colloidal dispersion stabilization	W. Germany 2,358,580	1975	Dow Chemical
Ester derivatives for Ag halide photographic emulsion stabilizer	W. Germany 2,436,185	1975	Fuji Photo Film
Emulsifier for electrostatic latex coatings	W. Germany 2,453,518	1975	Dow Chemical
Carpet cleaning resins	W. Germany 2,459,125	1975	Ciba-Geigy
Photographic emulsion dispersant	W. Germany 2,512,042	1975	Agfa-Gevaert
Cleaning, waxing, and polishing dispersant	W. Germany 2,522,091	1975	Procter & Gamble
Carpet cleaning resin dispersant	Japan 188	1975	3M Co.
Nonmigratory resin emulsifiers	United States 3,932,333	1976	Monsanto
Resin for carpet cleaning formulations	Canada 985,113	1976	Unilever Ltd.
Dispersant for PVC production	Belgium 847,631	1977	Nissan Chemical Industries
Half-ester emulsifiers for unsaturated polyesters	W. Germany 2,312,616	1977	Hoechst A.G.
Emulsion coating additives	W. Germany 2,654,915	1977	Nippon Zeon
Magnetic particle dispersant for recording tape	Canada 1,043,638	1978	Fuji Photo Film

Table A.2 (cont.)

Modifications/Applications	Patent	Year	Assignee
Rubber latex stabilizers	Britain 1,555,851	1979	Goodyear Tire & Rubber
Polymer and pigment dispersants	Europe 5,795	1979	Hoechst A.G.
Polymeric dispersant for diene polymers	E. Germany 134,355	1979	VEB Chemische-Werke
Suspension polymerization stabilizers	E. Germany 139,128	1979	F. Wolfe
Amine salts-polymer dispersants	W. Germany 2,823,301	1979	Hoechst A.G.
Non-migrating dispersing agents	W. Germany 2,841,562	1979	Rohner A.G.
Dispersant for Ag halide photographic emulsions	Japan 17,832	1979	Konishiroku Photo Ind.
Dispersant for direct positive photosensitive materials	Japan 18,936	1979	Mitsubishi Paper
Alkali metal, NH <sub>4</sub> , or amine derivatives as stabilizing dispersants	Japan 132,493	1979	Daiichi Kogyo Seiyoku Co.
Ag halide dispersant—photographic applications	U.S.S.R. 667,945	1979	All-Union Scientific Research Institute
Dispersant for recovery of oil from tar sands	U.S.S.R. 674,996	1979	Bashkir State Scientific Research Institute
Modifier for photographic Ag emulsion coatings	U.S.S.R. 702,337	1979	Belorussian State University
Dispersant for pigments, emulsifiers and protective colloid	United States 4,200,720	1980	Dow Chemical
Synthetic binder for photographic emulsions	Britain 1,565,359	1980	GAF Corp.
Salts for PVC emulsion production	W. Germany 2,263,181	1980	Wacker-Chemie G.m.b.H.
Ammonium salt as emulsifier	W. Germany 2,911,333	1980	Wacker-Chemie G.m.b.H.
Component in emulsion adhesives for building materials	Japan 5,939	1980	Yayoi Kagaku Kogyo Co.
Polymeric dispersants	Japan 22,489	1980	Kenki Kayaku Kogyo
Dispersant for pressure-sensitive copying paper resins	Japan 66,945	1980	Mitsui Toatsu Chemicals
Dispersant for PVC production	Japan 160,005	1980	Shinetsu Chemical
Textile bleaching bath additive	Romania 66,511	1980	Institut de Cercetari Textile
Amphoteric polyelectrolyte emulsifier	Romania 73,606	1980	Intr. Chim. Risnov



Table A.2 (cont.)

Modifications/Applications	Patent	Year	Assignee
Emulsion polymerization stabilizer	Europe 25,979	1981	Hoechst A.G.
<i>ELASTOMERS</i>			
Rubber additives for improved vulcanization properties	France 1,272,085	1962	Pneumatiques et Caoutchoue Manufacture
Rubber modifiers	Britain 1,184,764	1970	Cassella Farbenwerke
<i>ENZYME/MEDICINAL CARRIER</i>			
Barbituric acid derivative as hypnotic agent	Japan 11,552	1966	Shionogi
Pb and Sn derivatives as bactericidal coatings	U.S.S.R. 181,289	1966	P. I. Zobov
Enzyme binder (carrier) resins	W. Germany 1,943,490	1970	Monsanto
Enzyme carrier resins	W. Germany 1,948,177	1970	Monsanto
Enzyme binder (carrier) resins	W. Germany 1,944,369	1970	Yeda Research
Enzyme carrier resins	W. Germany 1,945,748	1970	Monsanto
<i>EPOXY RESIN HARDENER</i>			
Epoxy resin curing agents	W. Germany 1,033,047	1958	Badische Anilin
Epoxy resin modifier	United States 3,099,638	1963	Westinghouse Electric
Epoxy curing agent	United States 3,118,848	1964	Cook Paint & Varnish
Epoxy blends for metal coatings	United States 3,321,424	1967	Swift & Co.
Epoxy thermosetting resin blends	United States 3,417,045	1968	Dow Chemical
Epoxy thermosetting resin blends	United States 3,417,162	1968	Dow Chemical
Epoxy curing agent-modifier	Czechoslovakia 126,116	1968	I. Wiesner
Epoxy blends for thermosetting materials	France 1,531,763	1968	Dow Chemical
Epoxy crosslinker and modifier	United States 3,422,076	1969	American Cyanamid
Epoxy resin crosslinker	W. Germany 2,146,439	1972	Atlantic Richfield
Epoxy resin crosslinker	W. Germany 2,149,583	1972	Allied Chemical
Epoxy resin crosslinker	W. Germany 2,118,690	1973	Reichhold-Albert-Chemie
Epoxy resin modifiers and hardeners	Czechoslovakia 154,379	1974	P. Jarolimek

Table A.2 (cont.)

Modifications/Applications	Patent	Year	Assignee
Epoxy crosslinker for photographic subbing layers	W. Germany 2,349,494	1974	Fuji Photo Film
Epoxy hardener for dry transfer colorations of metallic surfaces	W. Germany 2,424,949	1974	Sublistatic Holding S.A.
Epoxy curing resins	United States 3,997,499	1975	Gulf Oil
Epoxy resin hardener for composites	Japan 153,098	1975	Sumitomo Bakelite
Epoxy resin hardeners	U.S.S.R. 448,742	1975	Institute of Petrochemical Process
Epoxy resin modifier for printed circuits	United States 3,985,928	1976	Sumitoma Bakelite
Epoxy crosslinker for coatings	United States 3,997,499	1976	Gulf Oil
Epoxy resin hardener for glass-fiber composites	W. Germany 2,537,195	1976	Gulf Oil
<i>FIBERS/FABRICS</i>			
Dye carrier resins	United States 2,389,575	1945	DuPont
Fiber modifier—spinning solution additive	United States 2,399,084	1946	DuPont
Amide derivatives in textile coatings	United States 2,456,177	1948	DuPont
Salts as textile sizing agents	United States 2,469,407	1949	Monsanto
Fiber coatings—asphalt moldings	United States 2,470,329	1949	Monsanto
Textile coatings	United States 2,486,804	1949	Henry H. Frede
Textile binder for diapers	United States 2,486,805	1949	Henry H. Frede
Water-repellent coatings	United States 2,524,022	1950	Montclair Research
Crosslinked resins in textile printing pastes	United States 2,533,635	1950	Monsanto
Esters as textile sizing agents	United States 2,576,915	1951	Monsanto
Epoxide derivatives as textile coatings	United States 2,607,761	1952	Chattanooga Research Institute
Fabric finishing derivatives	United States 2,609,350	1952	GAF Corp.
Textile sizing derivatives	United States 2,616,867	1952	Monsanto
Textile sizing agents	United States 2,630,416	1953	Stein, Hall & Co.
Dye carrier resins	United States 2,632,004	1953	Eastman Kodak
Salts as textile sizes	W. Germany 890,182	1953	Dynamit AKT
Wax blends for fiber coatings	United States 2,676,934	1954	Monsanto
Salt derivatives as textile fiber coatings	United States 2,686,103	1953	DuPont
Derivatives as textile sizing agents	United States 2,697,672	1954	Monsanto



Table A.2 (cont.)

Modifications/Applications	Patent	Year	Assignee
Textile finishes	United States 2,698,264	1954	Monsanto
Textile sizing and finishing agents	W. Germany 902,367	1954	Dynamit AKT
Ester derivatives as textile shrinkproofing coatings	W. Germany 906,685	1954	Dynamit AKT
Aid for PAN fiber production	United States 2,719,136	1955	Eastman Kodak
Resin dye carrier (binder)	United States 2,732,382	1956	Eastman Kodak
Amide derivatives as textile pigment fixers	France 1,124,128	1956	French Materials Pigments Co.
Salt derivatives as textile coatings	W. Germany 953,562	1956	Badische Anilin
Acid form as cellulose fiber modifier	W. Germany 1,016,892	1957	Badische Anilin
Modifier for cellulose fibers	United States 2,829,944	1958	DuPont
Derivatives as textile warp sizing materials	United States 2,845,689	1958	American Cyanamid
Salts as textile waterproofing coatings	W. Germany 1,062,664	1959	Chemische Fabrik Duren G.m.b.H.
Glass fabric sizing resins	United States 2,953,477	1960	Exeter Mfg.
Adhesives for textile laminates	W. Germany 1,101,348	1961	G. Honig
Salts as latex thickeners, warp sizing, rug backing materials	United States 3,030,342	1962	Koppers
Abrasion-resistant cotton fabric coatings	United States 3,084,070	1963	Jersey Production Research
Preparation as dry powder—textile coatings	Belgium 644,776	1964	Deering–Milliken
Modifier for paper-synthetic fiber blends	Belgium 645,911	1964	Fabriken A.G.
Polyester fiber modifier	France 1,386,045	1965	Kurashiki Rayon
Thermosetting filler, finishing agent for textiles, thickener and thixotropic additive	Netherlands 1,775	1966	Ciba Ltd.
Keratin fiber crosslinker	Netherlands 2,090	1966	Oreal S.A.
Aqueous salt as fabric softener	U.S.S.R. 179,878	1966	All-Union Scientific Research Institute
Textile soil-repellent coatings	Netherlands 10,041	1967	Deering–Milliken
Textile sizing agent	Britain 1,121,664	1968	Dan River Mills
Fire-retardant coatings	France 1,527,373	1968	Farbenfabriken
Fiber additive to improve dyeability	United States 3,423,481	1969	Tokuyama Soda Co.
Fugitive azo dye carrier	United States 3,449,319	1969	Deering–Milliken
Aqueous thickeners for dye solutions	W. Germany 1,904,309	1970	Diamalt A.G.
Pigment binder for textile printing	W. Germany 2,910,471	1970	Farbwerke Hoechst

Table A.2 (cont.)

Modifications/Applications	Patent	Year	Assignee
Crosslinked resin for synthetic hair	W. Germany 1,951,219	1970	Tokuyama Soda Co.
Dye carrier resins	W. Germany 2,027,537	1970	CIBA, Ltd.
Ester derivatives as textile fiber coatings	Japan 33,398	1970	Meisei Chemical Works
Textile coatings	United States 3,576,915	1971	Monsanto
Textile sizing agents	United States 3,585,070	1971	Monsanto
Sulfonated salts—additives for textile dyeing	W. Germany 1,959,051	1971	Farbenfabriken Bayer
Pigment binder for textile coatings	United States 3,634,131	1972	Deering-Milliken
Salt derivatives as textile sizing resins	Japan 611	1972	Omi Kenshi Spinning
Slip agent for textile	United States 3,726,820	1973	W. R. Grace
Nonwoven textile fabrics adhesives	United States 3,753,842	1973	Deering-Milliken
Imide copolymer for fiber sizing	Japan 42,630	1973	Omi Kenshi Spinning Co.
Cellulose web coatings	United States 3,808,161	1974	American Cyanamid
Imides for basic mordants	United States 3,876,429	1975	VEB Filmfabrik
Textile antistatic coatings	Japan 152,100	1975	Asahi Chemical Ind.
Water-repellant textile finishes	United States 4,070,152	1978	Ciba-Geigy
Wool dye assist agents	W. Germany 2,744,395	1979	BASF A.G.
Textile yarn sizing agents	United States 4,189,416	1980	Monsanto
Amine derivatives as dyeing retarders	Europe 13,540	1980	Ciba-Geigy A.G.
Modifier for fiber spinning	U.S.S.R. 761,501	1980	E. B. Avakyan
Antistatic coating for cellulose acetate fabric	U.S.S.R. 761,622	1980	F. A. Ismailov

*FILMS*

Color photography resins	Britain 569,646	1945	DuPont
Derivatives in photographic color film	United States 2,673,801	1954	Gevaert Photo Producten N.V.
Modified resins for photographic films	United States 2,816,028	1957	Eastman Kodak
Photographic film and paper modifier	United States 3,132,944	1964	Eastman Kodak
Photographic stripping film additives	Britain 960,050	1964	GAF Corp.
Photographic film anithalation layer	U.S.S.R. 173,602	1965	G. N. Lapshin
Radiation-curable materials	United States 3,281,263	1966	Dow Chemical
Black coatings for photographic film supports	France 1,539,752	1968	Fuji Photo Film



Table A.2 (cont.)

Modifications/Applications	Patent	Year	Assignee
Quaternary amide derivatives for photographic films	United States 3,488,706	1970	Eastman Kodak
Imide derivatives for packaging	W. Germany 1,806,269	1970	Farbenfabriken
Sulfonated resins for electrophotographic materials	W. Germany 1,926,561	1970	Mitsubishi Paper Mills
Photographic Ag complexes	W. Germany 2,005,042	1970	Ceskoslovenska Akademie Ved.
Ag halide dispersant for photographic emulsions	United States 3,615,624	1971	Eastman Kodak
Antistatic coatings for photographic films	W. Germany 2,011,649	1971	Agfa-Gevaert
Antistatic coatings for photographic films	United States 3,634,336	1972	Eastman Kodak
Na salt antistatic for films	U.S.S.R. 720,411	1980	Research Institute of Photographic-Chemical Industry
Optically transparent films	U.S.S.R. 755,801	1980	Kalinin State University

ION-EXCHANGE RESINS

Cation-exchange resins	United States 2,340,110	1944	General Electric
Salts—polyelectrolytes	United States 2,607,762	1952	Monsanto
Crosslinked resin in ion-exchange resins	United States 2,944,033	1960	S. Goodman
Crosslinked copolymers	W. Germany 1,094,463	1960	Asahi Chemical
Crosslinked materials as anion-exchange resins	W. Germany 1,151,124	1963	VEB Farbenfabrik Wolfen
Cation-exchange resins	W. Germany 1,155,603	1963	VEB Farbenfabrik Wolfen
Thickening agent, protective colloid, ion-exchange resins	France 1,466,860	1967	Oesterreichische Stickstoffwerke A.G.
Ion-exchange resins	France 1,483,946	1967	Dia-Prosim
Anion-exchange resin—paper coatings	France 1,568,491	1969	Dow Chemical
Crosslinked copolymer for cation-exchange resins	United States 3,586,646	1971	Farbenfabriken Bayer A.G.
Crosslinked amides for beer chill haze removal	United States 3,597,221	1971	Monsanto
Cation-exchange membrane	Britain 1,251,550	1971	Tokuyama Soda Co.
Crosslinked resin for cation exchange resins	U.S.S.R. 304,262	1971	S. B. Makarova
p-Hydroxystyrene copolymer polyion complexes for dialysis membranes	W. Germany 2,412,092	1974	Maruzen Oil

Table A.2 (cont.)

Modifications/Applications	Patent	Year	Assignee
Crosslinked resins for gel chromatography	U.S.S.R. 648,566	1979	Irkutsk State University
Chromatographic carrier for disulphide exchange reactions	U.S.S.R. 687,081	1979	A. V. Ilina

*LAMINATES*

Production procedures	United States 2,514,389	1950	Monsanto
Thermosetting resins	United States 2,519,764	1950	Monsanto
Crosslinked amides in laminates	United States 3,297,787	1967	Dow Chemical
Thermosetting laminate resins	United States 3,306,954	1967	Dow Chemical
Epoxy resin polyblend modifier	United States 3,322,853	1967	Monsanto
Asbestos coating and impregnating resin	W. Germany 1,232,935	1967	PPG
Thermosetting wire coatings, paper impregnants	United States 3,381,054	1968	Monsanto
Thermosetting laminating resins	France 1,517,845	1968	Dow Chemical
Crosslinked imides	W. Germany 1,956,285	1971	Badische Anilin
Imide derivatives for glass-fiber laminates	United States 3,632,791	1971	Dow Chemical
Decorative laminating resins	Japan 11,677	1972	Japan Catalytic
Glass fiber—styrene laminates adhesion promoter	W. Germany 2,160,778	1973	Badische Anilin
Glass-fiber coatings for composites	Japan 88,134	1973	Sumitomo Chemical
Polystyrene polyblends—laminated sheets	Japan 87,542	1980	Standard Oil
Laminated sheets	United States 4,251,591	1981	Monsanto
Poly(vinylbutyral) laminates	Europe 26,659	1981	Monsanto

*LEATHER MODIFIERS*

Sulfonated resins for leather modification	United States 2,452,536	1948	DuPont
Sulfonated resins as tannery auxiliary agents	United States 2,475,886	1949	DuPont
Salts for tanning limed skins	United States 2,707,667	1955	DuPont
Amide derivatives for leather dying	Netherlands 6,540	1966	Farbenfabriken Bayer A.G.



Table A.2 (cont.)

Modifications/Applications	Patent	Year	Assignee
Aqueous binder for artificial leather formulations	Czechoslovakia 143,150	1971	E. Mueck
Suede-type leather modifier	W. Germany 2,207,534	1972	State Research Institute of Kozedelny
Binder resin for artificial leather	Czechoslovakia 147,089	1973	L. Blazek
Leather polish dispersants	Japan 123,737	1975	Wilson Co.
<i>LITHOGRAPHIC PLATES</i>			
Hydrophilic binders for offset printing plates	W. Germany 2,165,358	1972	Mitsubishi Paper Mills
Photosensitive printing plate resins	W. Germany 2,251,030	1973	Fuji Photo Film
Presensitized resins for lithographic plates	United States 3,785,825	1974	Polychrome Corp.
Binder for di-azid lithographic printing plates	United States 3,802,885	1974	Algraphy, Ltd.
Photosensitive printing plate resins	Japan 44,801	1974	Oakamoto Chemical Ind.
Sensitized printing plate resins	W. Germany 1,797,587	1975	Hoechst A.G.
Barrier resins for offset printing plates	W. Germany 2,429,029	1975	Kanzaki Paper Mfg.
Azide derivatives for photo-resists, lithographic plates, radiation curable polymers	Japan 7,365	1977	Upjohn Co.
Photocurable compositions	Britain 2,011,431	1979	Somar MFS. Co.
Photosensitive lithographic printing plates	W. Germany 2,924,294	1979	Fuji Photo
<i>MEMBRANES</i>			
Crosslinked resins for membranes	United States 3,291,632	1966	PPG
<i>p</i> -Hydroxystyrene copolymer polyion complexes for dialysis membranes	W. Germany 2,412,092	1974	Maruzen Oil
<i>p</i> -Isopropenylphenol copolymer membrane complexes	United States 4,032,513	1977	Maruzen Oil
Crosslinked membrane	W. Germany 2,834,716	1979	Terumo Corp.
Crosslinked resins for gel chromatography	U.S.S.R. 648,566	1979	Irkutsk State University

Table A.2 (cont.)

Modifications/Applications	Patent	Year	Assignee
<i>METAL COMPLEXING/SEQUESTERING RESINS</i>			
Crosslinked resins as rare earth-metal absorbers	United States 2,471,818	1949	Dow Chemical
Pb and Sn derivatives as bactericidal coatings	U.S.S.R. 181,289	1966	P. I. Zobov
Sn and Pb derivatives for microbiocides, insecticides, and fungicides	Britain 1,101,929	1968	—
Modifier for battery Zn electrodes	U.S.S.R. 221,775	1968	Ivanovo Chem.-Tech. Inst.
Rare-earth metal oxide, carbonate binder resins	U.S.S.R. 243,080	1969	G. A. Vostrov
Photographic Ag complexes	W. Germany 2,005,042	1970	Ceskoslovenska Akademie Ved.
Crosslinked resins for virus separation and isolation	United States 3,655,509	1972	Monsanto
Heavy-metal collector resin	Japan 38,880	1973	M. Okamura
<i>N</i> -Bromoimide derivative resins as lead trap	United States 3,799,870	1974	Mobil Oil Corp.
Resins for K <sup>+</sup> recovery systems	W. Germany 2,318,107	1974	BASF A.G.
Crosslinked resins for sanitary products	W. Germany 2,405,981	1974	Dow Chemical
Separation media resins	U.S.S.R. 494,394	1975	Inst. Heteroorganic Compounds
<i>p</i> -Isopropenylphenol copolymer for heavy-metal scavenger ion-exchange resins	Japan 6,790	1977	Agency of Industrial Science
<i>p</i> -Isopropenylphenol copolymer for heavy-metal scavenger ion-exchange resins	Japan 6,791	1977	Agency of Industrial Science
Petroleum dewatering and desalting agent	U.S.S.R. 659,600	1979	All-Union Scientific Research Institute
<i>OIL ADDITIVES</i>			
Esters lube additives	United States 2,570,846	1951	Socony-Vacuum
Thiophene modified in lubricating oils	United States 2,600,798	1952	Socony-Vacuum
Esters as pour point depressants	United States 2,615,843	1952	Socony-Vacuum
Esters in lubricating oils	United States 2,654,727	1953	Socony-Vacuum
Esters in lubricating oils	United States 2,671,773	1954	Oil
			Socony-Vacuum



Table A.2 (cont.)

Modifications/Applications	Patent	Year	Assignee
Esters as grease additives	United States 2,698,297	1954	Socony-Vacuum Oil
Esters as viscosity index lubricating oils	United States 2,710,283	1955	Standard Oil of California
Ester derivatives—Polyisobutylene blends as stable greases	United States 2,737,494	1956	Socony Mobil
Metal salts in lubricating oils	United States 3,296,131	1967	Sinclair Research
Lubricating oil dispersant	United States 3,329,658	1967	Monsanto
Lubricating oil additive	United States 3,365,399	1968	Sinclair Research
Motor oil modifier	United States 3,432,479	1969	Sinclair Research
Esters as oil viscosity control agents	United States 3,449,250	1969	Monsanto
Amide-salt derivative as diesel fuel additive	United States 3,450,513	1969	Sinclair Research
Ester derivatives—pour point depressants	W. Germany 1,800,712	1969	Mobil Oil Corp.
Amide derivatives—detergent, ashless lubricating oil modifier	United States 3,493,520	1970	Sinclair Research
Emulsifiers for latex polymers amide-salt derivatives for diesel fuel additives	United States 3,505,156	1970	Imperial Chemical
Metallic salts for diesel fuel additives	United States 3,506,625	1970	Sinclair Research
Ester derivatives for metal working lubricants	United States 3,527,726	1970	Atlantic Richfield
Esters as lubricating oil pour point depressants	United States 3,536,461	1970	Sinclair Research
Esters for lubricating oils	W. Germany 1,963,761	1970	Lubrizol Corp.
Amine derivatives for ashless lubricating oil dispersants	United States 3,563,960	1971	Atlantic Richfield
Esters as lube oil modifiers	United States 3,574,575	1971	Mobil Oil
Salts of copolymer as additives in aqueous lubricating and cooling formulations	United States 3,629,112	1971	Atlantic Richfield
Amide-ester derivatives for lubricating oils	United States 3,933,761	1976	Lubrizol Corp.
Fuel oil flow-improving additives	Netherlands 10,661	1979	Exxon Research
<i>PLASTICS</i>			
Rubber modified—moldings	United States 2,275,957	1942	Rubber Production Assoc.
Moldings and coatings	United States 2,320,724	1943	PPG
Moldings	Canada 423,452	1944	U.G.I.
Plasticized resins	United States 2,407,413	1946	PPG

Table A.2 (cont.)

Modifications/Applications	Patent	Year	Assignee
Thermoplastics	United States 2,456,358	1948	Allied Chemical
Esters in thermosetting materials	United States 2,479,486	1949	PPG
Coatings and laminates	United States 2,516,309	1950	Monsanto
Salts as antistatic coatings for plastics	United States 2,912,413	1959	Monsanto
Modifier for epoxy resins	W. Germany 1,100,113	1961	Westinghouse Electric
Molding compositions	United States 3,046,246	1962	Texas Butadiene Chemical Corp.
Molding resins	United States 3,085,986	1963	Sinclair Research
Molding resins	France 1,366,979	1964	Y. Landler
Coating, molding, casting, and laminating resin blends	United States 3,225,115	1965	Union Carbide
Crosslinked amides in laminates	United States 3,297,787	1967	Dow Chemical
Polyol derivative for decorative coatings, moldings, and laminates	United States 3,336,259	1967	Dow Chemical
Thermosetting castings and moldings	United States 3,487,125	1969	Sinclair Research
Transparent, acid-resistant materials	France 2,010,152	1970	Scholven-Chemie A.G.
Grafting with lactams for molding materials	W. Germany 1,905,452	1970	Allied Chemical Corp.
Additives to reduce furan resin shrinkage	W. Germany 2,020,260	1971	Chemische Werke
Plastic foams for roof insulation	United States 3,672,951	1972	Dow Chemical
Crosslinked shaped articles	United States 3,678,016	1972	Dow Chemical
Fiberglass molding resins	United States 3,717,557	1972	Gulf Oil
Wood composite modifiers for plastics	United States 3,765,934	1972	Champion International Corp.
Carbon black molding resins	W. Germany 2,223,020	1972	Lobdell-Emery Mfg.
Imide derivatives for molding resins	United States 3,801,549	1974	Dow Chemical
Imide production procedures	W. Germany 2,343,408	1974	Sinclair Koppers
Thermosetting moldings	Japan 57,056	1974	Showa Highpolymers Co.
Unsaturated derivatives for electrically resistant moldings	Japan 110,732	1974	Showa Highpolymers Co.
Allyl esters in fire-resistant moldings	Japan 110,735	1974	Showa Highpolymers Co.
Electrophotographic recording resins	W. Germany 2,336,094	1975	Hoechst A.G.



Table A.2 (cont.)

Modifications/Applications	Patent	Year	Assignee
Thermosetting molding resins	W. Germany 2,421,556	1975	Gulf Research
Crosslinked moldings	United States 3,933,747	1976	Dow Chemical
Epoxy resin modifier for printed circuits.	United States 3,985,928	1976	Sumitomo Bakelite
Flame-retardant plastics and coatings	United States 4,032,509	1977	Monsanto
Thermoset moldings and coatings	Britain 1,488,198	1977	Gulf Oil
High-strength thermoplastic moldings	United States 4,097,550	1978	General Electric
Recording sheet binder resins	Japan 41,235	1978	Honshu Paper
Mold casting compositions	Japan 127,323(4)	1978	Hitachi, Ltd.
Imides as molding resins	United States 4,129,619	1979	ARCO Polymers
Impact-resistant thermoplastics	United States 4,137,281	1979	Standard Oil
Flame-retardant moldings	United States 4,151,218	1979	Monsanto
Impact-resistant moldings	Japan 50,553	1979	Sumitomo Chemical
Heat-sensitive recording sheet	Japan 70,553	1979	Fuji Photo Film
Electrophotographic flexible sheets	U.S.S.R. 614,415	1979	Organic Technical Design
Automotive linear panels	United States 4,188,440	1980	Van Dress Corp.
Binder for magnetic recording medium	Japan 73,929(30)	1980	TDK Electronics
Molding resins	Japan 112,213(14,15)	1980	Sekisui Plastics
Biodegradable plastics	Japan 157,643	1980	Nichiden Chemical
Crosslinked imide films	U.S.S.R. 759,545	1980	Institute of Hetero-organic Compounds
Thermoplastic molding blends	United States 4,243,766	1981	General Electric
<i>POLYMER ADDITIVES</i>			
Plasticizers	United States 2,359,103	1944	PPG
Chlorinated resins	United States 2,578,259	1951	U.S. Government
Salts as stabilizer for poly(vinylidene chloride)	United States 2,673,191	1954	B. F. Goodrich
Photographic emulsion stabilizer	United States 2,843,488	1958	Eastman Kodak
Waterglass cement and additives	W. Germany 1,062,856	1959	Farbwerke Hoechst
Ester derivative as polyurethane foam modifier	W. Germany 1,072,381	1959	Imperial Chemical
Modifier additive for phonograph record compositions	W. Germany 1,101,003	1961	Dynamit-Nobel
Polystyrene modifier	United States 2,971,939	1961	Monsanto

Table A.2 (cont.)

Modifications/Applications	Patent	Year	Assignee
Modifier for PVC foam	Belgium 627,414	1963	Y. Landler
Esters for detergent, cosmetics, and adhesives thickeners	Belgium 629,136	1963	GAF Corp.
Modifier-additive for polystyrene film	Belgium 631,039	1963	Dow Chemical
Esters as photographic film modifiers	Belgium 636,162	1963	Gevaert Photo Producten N.V.
Modifier for PVC foams	France 1,354,774	1964	Y. Landler
Polyester adhesive modifier	Netherlands 444	1964	Farbwerke Hoechst A.G.
Polyolefin-bitumen blend modifier	W. Germany 1,185,372	1965	Badische Anilin
Modifier for polystyrene foamed plastics	Belgium 671,085	1966	Dow Chemical
Foamed polystyrene modifier	Netherlands 5,797	1966	Imperial Chemical
Polishing composition additive	Netherlands 6,474	1966	Unilever N.V.
Amide derivatives as rubber bridging agents	United States 3,428,596	1969	Sinclair Research
Adhesive compositions	W. Germany 1,915,508	1969	Dow Chemical
Ester derivatives as PVA extenders	United States 3,492,254	1970	Sinclair Research
Ester derivatives in heat-resistant plastics	United States 3,509,110	1970	Koppers Co.
Ester derivatives as PVA plasticizers	United States 3,510,542	1970	Sinclair Research
Ester derivatives for plasticizers	W. Germany 1,806,270	1970	Farbenfabriken Bayer
PVC impact modifier	W. Germany 2,005,171	1970	Stauffer Chemical
Crosslinked resin for vinyl wax formulations	United States 3,554,949	1971	O. W. Burke, Jr.
Molding resin additives	United States 3,574,162	1971	Imperial Chemical
Antistatic additive for molded polystyrene	United States 3,574,790	1971	Sinclair Research
Ester derivatives as PVC stabilizers	United States 3,626,031	1971	Atlantic Richfield
Impact modifier for PVC	United States 3,626,033	1971	Dow Chemical
Modifier for polyolefin foams	Britain 1,220,053	1971	Imperial Chemical
Modifier for polyolefin foams	Britain 1,230,992	1971	Imperial Chemical
Resistor resin additive electric industry	Britain 1,241,302	1971	Matsushita
Modifier for thermoplastic polyolefin foams	France 2,036,830	1971	Imperial Chemical
Modifier for polystyrene	France 2,040,770	1971	Sinclair Koppers

Table A.2 (cont.)

Modifications/Applications	Patent	Year	Assignee
Thermoplastics impact modifier	W. Germany 1,949,487	1971	Badische Anilin
Thermoplastics molding modifier	W. Germany 1,950,599	1971	Badische Anilin
Transparent thermoplastic molding additive	W. Germany 2,024,940	1971	Badische Anilin
Amide for foam-cement combinations	Japan 16,519	1971	Omi Kenshi Spinning Co.
Metal salts for PVC stabilizers	United States 3,632,839	1972	Atlantic Richfield
Tin salts as PVC stabilizers	United States 3,640,973	1972	R. R. Chambers
Nitrile rubber impact modifier	United States 3,641,212	1972	Dow Chemical
Polystyrene impact modifier	United States 3,642,949	1972	Dow Chemical
Polystyrene additive for synthetic paper	United States 3,644,139	1972	Kimberly-Clark
Polyamide resin modifier	United States 3,644,571	1972	Gulf Research
Polybutadiene blends for plastics	United States 3,679,748	1972	Dow Chemical
Impact-resistant plastic additives	United States 3,689,596	1972	Dow Chemical
Flexible polymer formulations—sheet bonding	Czechoslovakia 146,692	1972	E. Mueck
PVC modifier	W. Germany 2,044,360	1972	Badische Anilin
Polycaprolactam modifier for laminates	W. Germany 2,049,380	1972	Badische Anilin
Component resins for foams	W. Germany 2,101,282	1972	Farbwerke Hoechst
Modifier for polystyrene laminates and films	W. Germany 2,119,934	1972	Badische Anilin
Water glass hardener	W. Germany 2,126,517	1972	Farbenfabriken Bayer
Derivatives for motar plasticizers	W. Germany 2,131,518	1972	Farbenfabriken Bayer
Carbon fiber resin adhesion promoter additive	W. Germany 2,212,789	1972	Atomic Energy Commission
Floor polish additives	United States 3,711,436	1973	Sinclair Koppers
Modified copolymer for coatings	W. Germany 2,137,105	1973	Reichhold-Albert-Chemie
Rubber modifier for impact-resistant plastic	W. Germany 2,246,726	1973	Dow Chemical
Degradative plastics composition resin	W. Germany 2,506,578	1973	A. Heslinga
Zinc salt derivative for toughening polystyrene film	Japan 46,671	1973	Asahi Dow
Modifier for SBR to give metal plating plastics	United States 3,896,252	1974	Dow Chemical
Thermoplastics impact modifier	W. Germany 2,245,957	1974	BASF A.G.



Table A.2 (cont.)

Modifications/Applications	Patent	Year	Assignee
Polycarbonate molding modifier	W. Germany 2,252,974	1974	Bayer A.G.
Modifier for improved polycarbonate moldings	W. Germany 2,304,894	1974	Bayer A.G.
Shrink reducer for unsaturated polyester resins	W. Germany 2,362,421	1974	Koppers Co.
Photographic film hardening agent	W. Germany 2,419,582	1974	Fuji Photo Film
Polyphenylene ether modifier	Japan 2,343	1974	Asahi Dow
Polyphenylene ether modifier	Japan 12,953	1974	Asahi Dow
Photographic film binders	Japan 135,619	1974	S. Nagotomo
Adhesives for metals bonding	U.S.S.R. 437,794	1974	Voronezh Tech. Inst.
Cellulosic composites modifier	United States 3,869,432	1975	Champion International Corp.
Modifier for impact-resistant plastics	United States 3,919,354	1975	Dow Chemical
Inorganic salt derivatives for Portland cement slurries	United States 3,923,717	1975	Dow Chemical
Crosslinked salt derivative PVC production	E. Germany 113,555	1975	F. Wolf and H. Karmer
Polycarbonate modifier	W. Germany 2,329,585	1975	Bayer A.G.
Stabilizer for ionomer salt preparations	W. Germany 2,338,642	1975	Hoechst A.G.
Composite filling resin	Japan 108,341	1975	Kyowa Chemical Ind.
Polamide modifier for coating formulations	U.S.S.R. 487,901	1975	Yaroslavl Polytechnic Institute
Modifier for starch-based adhesives	United States 3,939,108	1976	National Starch & Chemical
Polyamide moldings modifier	W. Germany 2,435,266	1976	BASF A.G.
Blends with styrene-butadiene-styrene block copolymers as impact-modified molding materials	W. Germany 2,713,455	1977	General Electric
Modifier for solid-state production of polyethylene terephthalate	Netherlands 3,890	1977	Chemische Werke Huels
Imides as polycarbonate modifier	Belgium 863,034(5)	1978	ARCO Polymers
Acrylamide-modified photoactive systems	Britain 1,498,726	1978	Fuji Photo Film
Additives and modifier for coatings	W. Germany 2,922,669	1979	PPG Industries

Table A.2 (cont.)

Modifications/Applications	Patent	Year	Assignee
Thermoplastics pigment binder	Japan 95,633	1979	Toyo Ink Mfg. Co.
Poly(phenylene oxide) modifier	United States 4,197,370	1980	General Electric
PPO modifier—foams	Britain 1,577,459	1980	General Electric
Modifier for impact-resistant nylons	Europe 10,938	1980	Monsanto
Production procedures for modified styrene resins with improved heat distortion	Japan 21,460	1980	Toray Industries, Inc.
Soil structure—property modifier	Japan 116,789	1980	Sekisui Chemical
Amine salts as butyl rubber modifier	U.S.S.R. 730,734	1980	Institute of Physical Chemistry
<i>PAPER MODIFIER</i>			
Paper coatings—mineral binders	United States 2,577,624	1951	Monsanto
Amide derivatives in paper coatings	W. Germany 876,035	1953	Dynamit-AKT
Ester and amide derivatives in paper coatings	United States 2,723,195	1955	Monsanto
Paper coatings	United States 2,897,111	1959	Monsanto
Paper coating resins	Belgium 619,443	1962	Imperial Chemical
Paper sizing resins	United States 3,103,462	1963	Eastman Kodak
Pressure-sensitive paper coatings	United States 3,104,980	1963	National Cash Register
Paper fiber sizing resins	Belgium 625,689	1963	Fabriken A.G.
Photographic film and paper modifier	United States 3,132,944	1964	Eastman Kodak
Half-amide salt as paper sizing resin	Netherlands 791	1965	Monsanto
Paper sizing agents	Netherlands 12,318	1965	Monsanto
Electrophotographic paper coatings	United States 3,241,958	1966	Addressograph-Multigraph Corp.
Sizing agent for paper	United States 3,243,398	1966	Monsanto
Sizing for photographic paper	United States 3,250,619	1966	Eastman Kodak
Sizing for cellulosic materials	United States 3,251,709	1966	Monsanto
Ammonium zirconyl carbonate crosslinked for paper coatings	Britain 1,029,055	1966	Inveresk Paper
Salt derivatives as paper coatings	United States 3,388,088	1968	Monsanto

Table A.2 (cont.)

Modifications/Applications	Patent	Year	Assignee
Paper sizing resins	United States 3,396,049	1968	Monsanto
Paper slip-coating resins	United States 3,400,008	1968	W. R. Grace
Amide-ester derivatives as starch modifier for paper sizing	United States 3,436,309	1969	Monsanto
Flame-retardant paper coatings	United States 3,454,588	1969	FMC Corp.
Paper sizing resins	United States 3,459,715	1969	Monsanto
Paper sizing formulations	France 1,560,904	1969	Polymer Corp.
Anion-exchange resin—paper coatings	France 1,568,491	1969	Dow Chemical
Paper—adhesives	France 1,583,641	1969	Farbenfabriken Bayer
Cationic starch binder	Britain 1,078,239	1970	National Starch & Chemical
Partial esters for paper coatings	W. Germany 1,938,162	1970	Ethyl Corp.
Copying paper coatings	W. Germany 1,944,883	1970	Arthur D. Little
Water-resistant paper coatings	Japan 16,815	1970	Japan Catalytic Chemical Ind.
Paper coatings	Britain 1,247,528	1971	Monsanto
Paper coatings formulation resin	Britain 1,252,630	1971	Mitsubishi Paper Mills
Paper sizing agents	W. Germany 2,007,790	1971	Schill and Seilacher
Paper sizing and finishing agents	W. Germany 2,042,430	1971	Schill and Seilacher
Polyolefin coatings for synthetic paper	W. Germany 2,107,408	1971	Japan Gas-Chemical
Electroconductive, solvent-resistant paper coatings	Japan 13,166	1971	Japan Pulp Ind.
Polystyrene additive for synthetic paper	United States 3,644,139	1972	Kimberly-Clark
Modifier for poly(ethylene-co-vinyl chloride) for paper and inks	United States 3,665,060	1972	Monsanto
Anionic paper sizing resins	W. Germany 2,034,263	1972	Farbenfabriken Bayer
Copying paper binder	W. Germany 2,224,954	1972	Schill and Seilacher
Ethylene-vinyl chloride polymer modifier for paper coatings	United States 3,755,219	1973	Monsanto
Anionic paper sizing resins	W. Germany 2,142,968	1973	Bayer A.G.
Electrostatic paper coatings resins	W. Germany 2,237,008	1973	Ricoh Co.
Dispersant for high-gloss paper coatings	W. Germany 2,310,891	1973	Star Paper, Ltd.
Paper sizing resins	Japan 41,003	1973	M. Takahara
Quaternized copolymer for antistatic paper coatings	Japan 43,473	1973	Ohji-Yuka Goseish Inc.



Table A.2 (cont.)

Modifications/Applications	Patent	Year	Assignee
Pressure-sensitive copying resins	Japan 51,715	1973	Fuji Photo Film
Salt derivatives for paper sizing agents	Japan 68,805	1973	Sumitomo Chemical
Ester derivatives for paper sizing agents	United States 3,792,119	1974	Monsanto
Ester derivatives for paper sizing agents	W. Germany 2,232,543	1974	Bayer A.G.
Thermoplastics impact modifier	W. Germany 2,245,957	1974	BASF A.G.
Amide derivatives as binder for paper staining colors	W. Germany 2,250,571	1974	Chemische Werke Huels
Alkali salts for paper coatings	W. Germany 2,413,922	1974	Toray Industries, Inc.
Microcapsule dispersion resins for copying paper	W. Germany 2,423,830	1974	Kanzaki Paper Mfg. Co.
Ester derivatives for photo-active copying materials	W. Germany 2,426,159	1974	Fuji Photo Film
Anionic paper sizing resins	W. Germany 1,621,693	1975	Bayer A.G.
Electrically conductive polysalt paper coatings	W. Germany 2,454,333	1975	Calgon Corp.
Resins for thermographic recording paper	Japan 30,539	1975	Mitsubishi Paper Mills
Photoresist resins	Japan 32,922	1975	Konishiroku Photo Ind.
Alkali-soluble paper substitute resins	Japan 118,004	1975	Denki Kagaku Kogyo
Pulp binder for wrapping paper production	U.S.S.R. 469,791	1975	Ukranian Scientific Research Institute
Paper sizing agents	Japan 23,997	1976	Sumitomo Chemical
Salt derivatives for paper sizing agents	U.S.S.R. 502,995	1976	Central Scientific Research Institute
$\alpha$ -Methylstyrene copolymer salts for paper sizing resins	U.S.S.R. 525,742	1976	Paper Research Institute
Polysalt complexes for electrically conductive paper coatings	United States 4,040,984	1977	Calgon Corp.
Paper coating resins	United States 4,048,422	1977	Bayer AKT
Binder for paper coatings	Japan 103,509	1977	Honshu Paper Mfg.
Hydrophilic fibers for paper-making	United States 4,154,646	1979	Hercules, Inc.
Hydrophilic fibers for paper	United States 4,158,595	1979	Hercules, Inc.
Paper coating pigment binders	Japan 22,226	1979	Honshu Paper
Ester derivatives as paper sizes	Japan 138,610	1979	Honshu Paper
NH <sub>3</sub> salt as anionic sizes for paper	Japan 11,800	1980	Bayer A.G.

Table A.2 (cont.)

Modifications/Applications	Patent	Year	Assignee
Sizes for paper for silicone coating	Japan 26,256	1980	Shikoku Paper Mfg. Co.
Recovery of polymer—sizing applications	Poland 104,629	1980	Instytut Wlokiennictwa
<i>POLYMER ALLOYS</i>			
Modifier for poly(phenyleneoxide) alloys	United States 4,221,880	1980	Arco Polymers, Inc.
Component of impact-resistant polyblend composition	Japan 7,849	1980	Dow Chemical
Polystyrene polyblends—sheet materials	Japan 71,530	1980	Mitsubishi-Monsanto
Polystyrene polyblends—laminated sheets	Japan 87,542	1980	Standard Oil
Thermoplastic molding blends	United States 4,243,766	1981	General Electric
<i>PRINTING INKS</i>			
Binder resin for printing dyes	United States 2,378,629	1944	DuPont
Printing poster resins	United States 2,686,736	1954	Sherwin-Williams
Photoactive resins for printing uses	United States 2,980,531	1961	Monsanto
Photoactive resins for printing uses	Britain 861,871	1961	Monsanto
Printing ink resins	United States 3,053,779	1962	Eastman Kodak
Imide derivative, dye transfer coatings	United States 3,184,309	1965	Eastman Kodak
Printing paste thickeners	W. Germany 1,902,811	1970	Chemische Werke
Ink binder resins	W. Germany 1,916,931	1970	Reichhold-Albert-Chemie
Photoresist printing pastes	Japan 1,678	1970	Research Institute Production Development
Binder resins for printing inks	United States 3,563,937	1971	Monsanto
Photosensitive printing plate resins	France 2,111,159	1971	Badische Anilin
Aqueous printing ink resins	Japan 29,041	1971	Seiko Chemical Ind.
Modifier for poly(ethylene-co-vinyl chloride) for paper and inks	United States 3,665,060	1972	Monsanto
Photosensitive printing plate resins	France 2,100,487	1972	Badische Anilin
Ink binder resins	W. Germany 2,136,055	1972	A.B. Dick, Co.
Ink binder resins	W. Germany 2,215,267	1973	Reichhold-Albert-Chemie

Table A.2 (cont.)

Modifications/Applications	Patent	Year	Assignee
Ink binder resins	W. Germany 2,215,268	1973	Reichhold-Albert-Chemie
Water-based ink binders	Japan 0,003	1974	Kyokoto Shibosan Co.
Vinyl toluene ink resins	Japan 29,122	1974	Toyo Ink Mfg. Co.
Offset printing ink binder	United States 3,903,034	1975	A.B. Dick Co.
Adhesives and printing ink binder	Japan 3,098	1977	Reichhold-Albert-Chemie
Modifier for white ink compositions	Japan 38,839	1980	Pentel Pen Co.
PROTEIN FIXING AGENTS			
N-Hydroxyimide derivatives for peptide synthesis	United States 3,488,329	1970	Monsanto
Crosslinked resins as selective separation medium for proteins	W. Germany 2,206,076	1970	Monsanto
Resin substrate for polypeptide synthesis	Japan 32,988	1973	Mitsubishi Chemical Ind.
Resin substrate for polypeptide synthesis	Japan 32,989	1973	Mitsubishi Chemical Ind.
Peptide chain activator	U.S.S.R. 759,545	1981	As USSR Element
SEALANTS/CAULKS			
Sealants for construction materials	Netherlands 6,780	1966	Bergwerksverband
Windshield, swimming tanks, etc., sealant	United States 3,462,516	1969	Phillips Petroleum
WATER-SOLUBLE POLYMERS			
Salts—polyelectrolytes	United States 2,607,762	1952	Monsanto
Salts as drilling mud additives	United States 2,718,497	1955	Union Oil of California
Flocculants for oil well drilling muds	United States 2,847,403	1958	Monsanto
Ester polyelectrolyte concrete mix additives	Australia 218,745	1958	Commonwealth Industries Research Organization
Soil conditioner additives	United States 2,872,436	1959	Dow Chemical
Enteric coating resins	United States 2,897,121	1959	Upjohn
Waterborne iodine carrier	Britain 824,215	1959	GAF Corp.
Protective coatings for drugs	W. Germany 1,063,758	1959	Upjohn
Ester derivatives as secondary oil recovery additives	United States 3,025,237	1962	Jersey Production Research



Table A.2 (cont.)

Modifications/Applications	Patent	Year	Assignee
Amide and ester derivatives as water thickeners—tertiary oil recovery additives	United States 3,070,158	1962	Jersey Production Research
Sulfonated resins as soil conditioners	United States 3,078,241	1963	Dow Chemical
Secondary oil recovery additives	United States 3,079,336	1963	Jersey Production Research
Amide derivatives in hair waving formulations	Belgium 629,769	1963	Oreal S.A.
Medicinal tablet coatings	United States 3,132,075	1964	Upjohn
Hair waving resins	Belgium 646,681	1964	Oreal S.A.
Alkali salts as polyelectrolytes	Czechoslovakia 109,809	1964	O. Peroutka
Medicinal tablet coatings	Britain 1,005,424	1965	Abbott Laboratories
Salt derivatives for tertiary oil recovery additives	United States 3,282,337	1966	Dow Chemical
Enteric tablet coatings	United States 3,282,790	1966	Upjohn
Aqueous thickeners	Netherlands 4,619	1966	Imperial Chemical
Drilling fluid viscosity control additive	United States 3,332,872	1967	Monsanto
Polyelectrolyte protective colloids	E. Germany 62,915	1968	H. Pobloth
Amide-acid derivative—organic gelled liquids	Britain 1,230,973	1969	Dow Chemical
Amide-acid derivatives—organic gelled liquids	France 1,572,688	1969	Imperial Chemical
Water-dispersible flocculant for suspended inorganic solids	United States 3,492,225	1970	Nalco Chemical
Flocculant	United States 3,492,226	1970	Nalco Chemical
Plaster additives to control viscosity	United States 3,544,344	1970	Sinclair Research
Encapsulation resin for lipophilic liquids, fertilizers, pesticides	United States 3,549,555	1970	National Cash Register
Aqueous thickeners for dye solutions	W. Germany 1,904,309	1970	Diamalt A.G.
Salts of crosslinked resins as thickeners	W. Germany 1,928,868	1970	Chemische Werke Huels
Waste water flocculant resin	W. Germany 1,945,749	1970	Monsanto
Gypsum paste additive setting time modifier	United States 3,563,930	1971	Sinclair Research
Polyelectrolytes	United States 3,554,985	1971	Monsanto
Plaster formulation additive to control viscosity	United States 3,563,777	1971	Sinclair Research

Table A.2 (cont.)

Modifications/Applications	Patent	Year	Assignee
Crosslinked resin for thickeners and protective colloids	Japan 34,620	1971	Research Institute Production Development
Salt derivatives as waste water flocculants	U.S.S.R. 302,315	1971	L. I. Shmidt
Waste water flocculants	United States 3,697,420	1972	D. S. Blaisdell
Silica composition viscosity control agents	United States 3,718,614	1973	American Cyanamid
Sulfonic acid derivative for oil well drilling muds	United States 3,730,900	1973	Milchem Inc.
<i>p</i> -Hydroxystyrene copolymer as polyelectrolyte resins	Japan 53,283	1974	Maruzen Oil
Flocculant for paper waste removal from water	W. Germany 1,595,333	1975	BASF A.G.
Water-soluble derivatives for coatings	Japan 47,827	1977	Hitachi Chemical
Amide derivatives as polyelectrolytes	U.S.S.R. 532,605	1977	UZB Chem.
Salts as ore grinding aids	United States 4,136,830	1979	Dow Chemical
Dispersant for recovery of oil from tar sands	U.S.S.R. 674,996	1979	Bashkir State Scientific Research Institute

Table A.3. Olefin-MA Copolymer Patents

Applications	Olefins	Patent	Year	Assignee
PRODUCTION PROCEDURE				
Production procedure	5-Methylene [2.2.1]hept-2-ene	United States 3,143,533	1964	Dow Chemical
Production procedures	Ethylene	France 1,360,001	1964	Badische Anilin
Production procedures	Ethylene	Austria 242,361	1965	Oesterreichische
Production procedure	1,5-Cyclooctadiene	Britain 1,000,670	1965	D. Bryce-Smith
Production procedure	1,5-Cyclooctadiene	Britain 1,015,215	1965	PPG
Production procedure	Ethylene, 2-methyl-1-pentene	Netherlands 294,518	1965	Imperial Chemical
Production procedure	Isoprene	Japan 26,704	1967	Toyo Rayon
Production procedure	Vinylcyclohexane	U.S.S.R. 203,895	1967	Institute of Petrochem Synthesis
Production procedures, flexible films, glass adhesives	Isoprene, chloroprene, butadiene, piperylene	United States 3,491,068	1970	Borg-Warner
Production procedure	Butadiene	Canada 848,513	1970	Borg-Warner
Production procedure	Butadiene	Canada 852,293	1970	Borg-Warner
Production procedure	3a,4,5,6,7,7a-hexahydro-4,7- methanoindene	Japan 30,828	1970	Hitachi Chemical
Production procedure coatings	Trans-1,2-bis(3-cyclohexene-1-yl) ethylene	United States 3,600,384	1971	Phillips Petroleum
Production procedure	Butadiene	Canada 867,843	1971	Borg-Warner
Decarboxylated copolymer	Ethylene	United States 3,682,868	1972	Rheinpreussen
Production procedure	Butadiene	United States 3,773,727	1973	Borg-Warner
Production procedures	1,5,9-Cyclododecatriene	Japan 14,866(7)	1974	Asahi Chemical
Suspension copolymerization pro- cedure	$\alpha$ -Olefins	Britain 1,528,992	1978	Bayer
Production procedure with ZnCl <sub>2</sub>	Isoprene	Romania 63,691	1978	Combinatul Petrochemic
Production procedure	C <sub>2</sub> -C <sub>8</sub> $\alpha$ -Olefins	U.S.S.R. 576,324	1978	Bayer
Production procedure	Dicyclopentadiene	United States 4,168,359	1979	Borg-Warner
Production procedure	Butadiene	Japan 48,886	1979	Nippon Oil
Production procedure with alkenylsuccinic anhydrides	Isobutylene	Japan 154,486	1979	Nippon Zeon



Production procedure with EVA copolymer dispersant	C <sub>4</sub> –C <sub>6</sub> $\alpha$ -Olefins	Japan 156,092	1979	Nippon Zeon
Production procedure with atactic polypropylene dispersant	C <sub>4</sub> –C <sub>6</sub> $\alpha$ -Olefins	Japan 156, 093	1979	Nippon Zeon
Compositions production procedure	Cyclopentadiene methylcyclopentadiene	United States 4,202,955	1980	Borg–Warner
Production procedure using poly(alkyl vinyl ethers)	C <sub>6–10</sub> alkenes	Europe 9,169	1980	BASF
Production procedure at elevated temperatures	2,4,4-Trimethyl pentene-1 or -2	Europe 9,170	1980	BASF
Production procedure	Norbornene	W. Germany 1,948,198	1980	Henkel KG
Production procedure using poly(alkyl vinyl ether) dispersants	C <sub>6–10</sub> alkenes	W. Germany 2,840,501	1980	BASF A.G.
Production procedures	2,4,4-Trimethyl-1-pentene or -2-pentene	W. Germany 2,840,502	1980	BASF A.G.
Powder polymer production	Ethylene	United States 4,243,784	1981	Hitachi Chemical
Powdered resin	Dicyclopentadiene	W. Germany 2,941,589	1981	Chemische Werke Huels
Powdered resins	$\alpha$ -Olefins	Japan 10,925	1981	Hitachi Chemical
Use of Diels–Alder adducts	Butadiene	Japan 17,368	1981	Borg–Warner

ADHESIVES

Coatings, surfactants, adhesives	Butadiene	Belgium 617,612	1962	Shell International
Hot melt ahesives	Ethylene	Belgium 618,156	1962	DuPont
Epoxy crosslinker, thermosetting resins	Ethylene	Japan 7,141	1963	Japan Catalytic
Pressure-sensitive adhesives	Butadiene	United States 3,205,088	1965	3M Company
Adhesives, coatings	1,1,4,4-Tetralkyl-1,3-butadiene	United States 3,250,751	1966	Eastman Kodak
Laminating adhesives	Ethylene	United States 3,419,461	1968	DuPont
Wood adhesives	Ethylene	Britain 1,155,004	1969	Monsanto
Production procedures, flexible films, glass adhesives	Isoprene, chloroprene, butadiene, piperylene	United States 3,491,068	1970	Borg–Warner
Coatings, adhesives	Ethylene	United States 3,578,641	1971	Monsanto

Table A.3 (cont.)

Applications	Olefins	Patent	Year	Assignee
Adhesives	Butenes	W. Germany 2,215,815	1971	Kuraray
Metal adhesives	1-Hexene	United States 3,637,579	1972	Gulf Research
Adhesives, coatings, moldings	1-Methyl-cyclopropene	United States 3,644,301	1972	Shell
Plastics, glass, metals, adhesives	Ethylene	Belgium 780,964	1972	Ethylene-Plastique
Adhesives for glass, metals, plastics	Ethylene	France 2,130,560	1972	Ethylene-Plastique
Adhesives	Propylene	France 2,132,383	1972	Kuraray
Adhesives, coatings	<i>cis</i> -piperylene, <i>trans</i> -piperylene	W. Germany 2,139,045	1972	Japanese Geon
Wood adhesives	Ethylenè, isobutylene	Japan 27,241	1972	Asahi Chemical
Plywood adhesives	Ethylene	Japan 27,242	1972	Kuraray
Carton sealing adhesives	Ethylene	United States 3,730,925	1973	Anheuser-Busch
Metal adhesives	Ethylene	W. Germany 2,214,331	1973	Ethylene-Plastique
Corrugated board adhesives	Isobutylene	Japan 8,327	1973	Kuraray
Wood adhesives	Isobutylene	Japan 42,032	1973	Kuraray
Adhesives, pigment dispersant, detergent additives	1-butene	Japan 42,094	1973	Kuraray
Plywood adhesives	Isobutene	Japan 91,136	1973	Kuraray
Wood adhesives	Isobutylene	W. Germany 2,354,362	1974	Kuraray
Plywood adhesives	Isobutylene	Japan 3,456	1974	Kuraray
Wood and paper adhesives	Isobutylene	Japan 8,534	1974	Kuraray
Plywood adhesives	Isobutene	Japan 8,537	1974	Kuraray
Wood adhesives	Isobutylene	Japan 25,026	1974	Kuraray
Wood adhesives	Isobutylene	Japan 25,027	1974	Kuraray
Plywood adhesives	Isobutylene	Japan 25,029	1974	Kuraray
General purpose adhesives	Isobutylene	Japan 25,030	1974	Kuraray
General purpose adhesives	Isobutylene	Japan 25,031	1974	Kuraray
Wood adhesives	Isobutylene	Japan 25,349	1974	Kuraray
Water-based wood adhesives	Isobutylene	Japan 26,342	1974	Kuraray
Wood adhesives	Isobutylene	Japan 26,356	1974	Kuraray
Wood adhesives	Isobutylene	Japan 28,629	1974	Kuraray
Paper and textile adhesives	Isobutylene	Japan 34,181	1974	Kuraray

Paper adhesives	Isobutylene	Japan 34,182	1974	Kuraray
Paper adhesives	Isobutylene	Japan 34,183	1974	Kuraray
Adhesive for abrasive polishing fabric	Isobutylene	Japan 34,184	1974	Kuraray
Adhesives for paper	Isobutylene	Japan 34,185	1974	Kuraray
Asbestos cement plate adhesives	Isobutene	Japan 45,927	1974	Hohnon Oil
General purpose adhesives	Isobutylene	Japan 47,892	1974	Kuraray
Wood adhesives	Isobutylene	Japan 64,670	1974	Kuraray
Adhesives compositions	Isobutylene	Japan 73,448	1974	Kuraray
Thermosetting adhesives, moldings	Ethylene, propylene, 1-butene	Japan 82,336	1974	Kuraray
Plywood adhesives	Isobutylene	Japan 92,154	1974	Kuraray
Aqueous plywood adhesives	Isobutylene	Japan 93,445	1974	Kuraray
Adhesives	Isobutylene	Japan 93,449	1974	Kuraray
Wood adhesives	Isobutylene	Japan 93,451	1974	Kuraray
Wood adhesives	Isobutylene	Japan 93,454	1974	Kuraray
Aqueous adhesives	Butadiene	Japan 108,140	1974	Nippon Oil
Plywood adhesives	Isobutylene	Japan 131,243	1974	Kuraray
Wood adhesives	Isobutylene	Japan 96,634	1975	Nippon Oils and Fats
Aqueous plywood adhesives	Isobutylene	Japan 100,122	1975	Nippon Oils and Fats
General purpose adhesives	Isobutylene	Japan 126,038	1975	Nippon Oils and Fats
SBR emulsifier, wood adhesives	Isobutylene	Japan 126,039	1975	Nippon Oils and Fats
Wood adhesives	Isobutylene	Japan 109,229	1975	Kuraray
Adhesives	Isobutylene	Japan 119,842	1975	Kuraray
Adhesives	Isobutylene	Japan 124,980	1975	Kuraray
Aqueous wood adhesives	Isobutene	Japan 132,108	1975	Hohnon Oil
Adhesives, coatings	Isobutylene	Japan 148,503	1975	Sumitomo Chemical
General purpose adhesives	Isobutylene	Japan 160,388	1975	Kuraray
Water-soluble adhesives, thick- eners, binders, coatings	Butadiene, isoprene	W. Germany 2,547,556	1976	Nippon Oil
Adhesives	Butadiene	Japan 127,189	1976	Nippon Oil
Release agent—pressure-sensitive adhesive tape	C <sub>6</sub> –C <sub>26</sub> $\alpha$ -olefins	United States 4,029,843	1977	Borden, Inc.
Water-soluble adhesives	Butadiene	United States 4,059,555	1977	Nippon Oil
Coatings, adhesives	Ethylene	Japan 132,091	1977	Kansai Paint



Table A.3 (cont.)

Applications	Olefins	Patent	Year	Assignee
Release agents adhesives	Ethylene	United States 4,076,666	1978	Formica Corp.
Reversible resins, aqueous adhesives thickeners, binders, coatings	Butadiene, isoprene	Britain 1,525,004	1978	Nippon Oil
Reversible resins, adhesives, thickeners, fire extinguisher additive	Butadiene, isoprene	Japan 20,075	1978	Nippon Oil
Coatings, adhesives	Ethylene, propylene, isobutylene, pentene-1	Japan 20,554	1978	Hitachi Chemical
Coatings, adhesives	Ethylene, propylene, isobutylene, pentene-1	Japan 20,555	1978	Hitachi Chemical
Aqueous adhesives	Isobutylene	United States 4,041,940	1979	Konishi
Adhesives	Isobutylene	Japan 41,940	1979	Konishi
Carpet backing compositions	2-Methyl-1-butene	Japan 68,497	1979	Japan Synthetic Rubber
Water-soluble adhesives	Isobutylene	Japan 95,639	1979	Ishikawa Sangyo
Adhesive additive	$\alpha$ -Olefins	Europe 21,694	1980	Monsanto
Water-resistant wood adhesives	Isobutylene	Japan 1,950	1980	Kuraray
Plywood adhesives	Ethylene	Japan 67,456	1980	Naniwa Plywood
Metal adhesive compositions for polyolefins	Cycloolefins	Japan 78,038	1980	Mitsubishi Petrochemical
Metal salts	Butadiene	Britain 1,583,154	1981	Nippon Oil
Water borne	Butadiene	Japan 10,951	1981	Daiichi Kogyo

BOILER SCALE CONTROL AGENT

Boiler scale remover agents	Ethylene	United States 2,723,956	1955	National Aluminate Corp.
Scale inhibitor, cleaning agent	Ethylene	United States 3,679,592	1972	Monsanto
Polyanionic boiler scale inhibitor agent	Ethylene	Britain 1,575,173	1980	American Cyanamid

CELLULAR MATERIALS

Thermal insulation product	Diisobutylene	United States 3,100,156	1963	Owens-Corning
Cellular plastics	1,3-Pentadiene	Britain 1,074,571	1967	BTR Industries
Insulating foams, wire coatings	Isobutylene, ethylene	W. Germany 1,811,166	1970	Farbenfabriken Bayer A.G.
Heat-resistant cellular plastics	Isobutylene	W. Germany 2,020,301	1971	Farbenfabriken Bayer A.G.
Insulating foams	Isobutylene	W. Germany 2,025,894	1971	Farbenfabriken Bayer A.G.
Foams	Isobutylene	W. Germany 2,056,358	1972	Farbenfabriken Bayer A.G.
Insulating foams	Isobutylene	W. Germany 2,027,985	1971	Farbenfabriken Bayer A.G.
Foamable polymeric alloy compositions	Ethylene	United States 4,207,402	1980	Monsanto

COATINGS

Water-soluble resins	Ethylene diisobutylene	Britain 562,092	1944	DuPont
Molding compounds, coatings, packaging films	Diisobutylene, 2-methyl-1-heptene	United States 2,373,067	1945	Standard Oil
Alkali-soluble resins	Ethylene, propylene, diisobutylene, isobutylene, 2,4,-trimethyl-1-pentene	United States 2,378,629	1945	DuPont
Alkali-soluble resins	Ethylene, propylene	United States 2,396,785	1946	DuPont
Decorative coatings	Diisobutylene	United States 2,865,877	1958	Rohm & Haas
Wood, paper, glass coatings	Diisobutylene	United States 2,865,878	1958	Rohm & Haas
Fungus-resistant fruit coatings	Ethylene	United States 2,883,287	1959	Monsanto
Photographic coatings	Ethylene	Britain 815,956	1959	GAF
Hair spray resins	Ethylene	United States 2,957,838	1960	Monsanto
Hair spray resins	Ethylene	Britain 839,805	1960	Monsanto
Specialty coatings	Ethylene	United States 2,977,334	1961	Monsanto
Decorative coatings	Diisobutylene	United States 2,971,934	1961	Rohm & Haas
Specialty coatings	1-Methyl-3-methylene cyclobutene	United States 2,995,543	1961	DuPont
Varnish and impregnant resins	Indene	W. Germany 1,110,416	1961	Bergwerksverband
Polyolefin coatings	Ethylene, propylene	United States 3,018,195	1962	Monsanto
Rubbery coatings	Ethylene	United States 3,040,006	1962	Monsanto
Paper sizing, adhesives, waxes, polishes, coatings	Isobutylene	United States 3,053,814	1962	Monsanto

Table A.3 (cont.)

Applications	Olefins	Patent	Year	Assignee
Coatings, surfactants, adhesives	Butadiene	Belgium 617,612	1962	Shell International
Metal coatings	Butadiene	United States 3,081,283	1963	Cities Service
Medicinal coatings	Ethylene	Belgium 622,793	1963	Eli Lilly
Hair treatment products	Ethylene, propylene, butenes	Belgium 629,437	1963	Colgate-Palmolive
Photographic coatings	Ethylene	Belgium 630,170	1963	Agfa A.G.
Specialty coatings	Isobutene, 2-methyl-1-butene	Britain 1,044,976	1963	Imperial Chemical
Epoxy crosslinker, thermosetting resins	Ethylene	Japan 7,141	1963	Japan Catalytic
Pigment binder	Ethylene	United States 3,127,362	1964	Monsanto
Hair wave solutions	Ethylene	United States 3,130,127	1964	John H. Breck, Inc.
Hair spray resins	Ethylene	United States 3,156,664	1964	Monsanto
Hair waving solutions, keratin fiber modifier	Ethylene	Belgium 646,681	1964	Oreal S.A.
Hair wave solutions	Ethylene	Belgium 665,342	1965	Oreal S.A.
Pigment coating for polyolefins	Ethylene	France 1,402,418	1965	Badische Anilin
Photographic films	Ethylene	W. Germany 1,191,688	1965	Polaroid
Image receptor coating—photo-graphic film	Ethylene	Netherlands 4,758	1965	Polaroid
Hair wave solutions	Ethylene	Netherlands 7,939	1965	Oreal S.A.
Synthetic drying oils	Butadiene	U.S.S.R. 170,598	1965	A. A. Subbotin
Adhesives, coatings	1,1,4,4-Tetralkyl-1,3-butadiene	United States 3,250,751	1966	Eastman Kodak
Specialty coatings	Ethylene	United States 3,255,143	1966	PPG
Epoxy resin curative	1,5-Cyclooctadiene	United States 3,261,815	1966	PPG
Wire coatings	Ethylene	United States 3,272,771	1966	DuPont
Gelatin hardeners—photographic films	Ethylene	United States 3,277,030	1966	Eastman Kodak
Specialty coatings	Ethylene, dicyclopentadiene	Netherlands 1,207	1966	Farbwerke Hoechst
Photographic films	Ethylene	United States 3,296,155	1967	Eastman Kodak
Photographic films	Ethylene	United States 3,308,075	1967	Eastman Kodak
Ink receptive coatings	Diisobutylene	United States 3,318,721	1967	Phillips Petroleum



Gelatin hardener—photographic films	Ethylene	United States 3,330,664	1967	Eastman Kodak
Wire coatings	Ethylene	United States 3,355,319	1967	DuPont
Steel plate coatings	Ethylene	W. Germany 2,248,867	1967	Dulux Australia
Thermosetting waterborne resins	Ethylene	Netherlands 10,969	1967	National Starch
Silver image coatings—photo-graphic films	Ethylene	Netherlands 12,967	1967	Polaroid
Radiant energy absorbers	Ethylene	United States 3,361,186	1968	Monsanto
Image receiving coatings, photo-graphic films	Ethylene	United States 3,376,137	1968	Polaroid
High-gloss waterborne enamels	Diisobutylene	Britain 1,109,656	1968	DuPont
Photosensitive coatings, litho-graphic printing plates	Ethylene	Britain 1,135,082	1968	Algraphy Ltd.
Thermosetting resins—epoxide blends	1-Hexene	France 1,513,981	1968	Gulf Research
Glass container coatings	Ethylene	France 1,542,147	1968	Libby-Owens-Ford
Nail polishes	Ethylene	France 1,547,495	1968	Oreal S.A.
Glass container coatings	Ethylene	South Africa 6,219	1968	Libby-Owens-Ford
Thermosetting resins	1-Hexene	United States 3,441,543	1969	Gulf Research
Carbonless coated capsules	Ethylene	France 1,565,952	1969	National Cash Register
Wax paper coatings	Ethylene, propylene, butenes, octenes, 1,4-hexadiene	France 2,001,144	1969	DuPont
Hair spray resins, medicinal coatings	Ethylene	W. Germany 1,930,009	1969	Monsanto
Thermoset resins	Ethylene	Japan 31,824	1969	Sumitomo Chemical
Floor polishes	1-Hexene	United States 3,488,311	1970	Gulf Research
Paper sizing polyolefin coatings	Diisobutylene	United States 3,494,783	1970	Phillips Petroleum
Specialty coatings	1-Hexene	United States 3,531,547	1970	Gulf Research
Floor polishes	1-Hexene, 1-decene, 1-octene	United States 3,532,656	1970	Gulf Research
Photoactive resins	Ethylene	France 2,009,112	1970	GAF Corp.
Insulating forms, wire coatings	Isobutylene, ethylene	W. Germany 1,811,166	1970	Farbenfabriken Bayer A.G.
Coatings	Ethylene	W. Germany 2,024,131	1970	Ethylene-Plastique S.A.
Thermoset resins	1-Hexene	United States 3,553,153	1971	Gulf Research
Coatings, adhesives	Ethylene	United States 3,578,641	1971	Monsanto
Thermoset moldings	1-Hexene	United States 3,594,354	1971	Gulf Research
Floor polishes	1-Hexene	United States 3,598,778	1971	Gulf Research

Table A.3 (cont.)

Applications	Olefins	Patent	Year	Assignee
Production procedure—coatings	Trans-1,2-bis(3-cyclohexene-1-yl)ethylene	United States 3,600,384	1971	Phillips Petroleum
Hair dye resins	Ethylene	United States 3,630,654	1971	Brystol-Meyers
Free films, coatings	Butadiene, isoprene chloroprene, piperylene, 2,3-dimethylbutadiene, 2,4-hexadiene	Britain 1,238,934	1971	Borg-Warner
Thermoplastics moldings, coatings	4-Vinylcyclohexene	Britain 1,255,838	1971	BP Chemicals
Light-sensitive photographic films	Ethylene	W. Germany 2,037,931	1971	Polaroid
Photographic films	Ethylene	W. Germany 2,038,260	1971	Polaroid
Waterborne resins	Diisobutylene	W. Germany 2,115,430	1971	Rohm & Haas, G.m.b.H.
Antistatic coatings	Diisobutylene	W. Germany 2,116,258	1971	Fuji Photo Film
Coatings	1-Butene, isobutene	W. Germany 2,119,677	1971	Kuraray
Thermoset resins	1,4-Hexadiene	Japan 39,235	1971	Toray Industries, Inc.
Thermosetting resins	C <sub>3</sub> -C <sub>20</sub> $\alpha$ -olefins	United States 3,647,923	1972	Gulf Research
Metal powder production aid	Ethylene	United States 3,694,185	1972	Sherritt Gordon Mines
Radiation-curable resins	Ethylene	United States 3,703,402	1972	General Electric
Coatings	5-Vinyl-2-norbornene	United States 3,703,501	1972	Celanese Coatings
Abrasive polishing capsules	Ethylene	France 2,109,995	1972	Engis Ltd.
Metal powder binder	Ethylene	W. Germany 2,132,173	1972	Sherritt Gordon Mines
Adhesives, coatings	<i>cis</i> -peperylene, <i>trans</i> -piperylene	W. Germany 2,139,045	1972	Japanese Geon
Antistatic resins—photographic films	Isobutylene	W. Germany 2,144,286	1972	Fuji Photo Film
Textile, metal and glass coatings	Ethylene	W. Germany 2,214,450	1972	Ethylene-Plastique
Thermosetting resins	2,4-Hexadiene	Japan 17,627	1972	Toray Industries, Inc.
Coatings	Butenes	United States 3,720,651	1973	Kuraray
Magnetic carrier coatings	C <sub>2</sub> -C <sub>10</sub> $\alpha$ -olefins	France 2,176,899	1973	Eastman Kodak
Concrete coatings	Ethylene	W. Germany 2,152,876	1973	Lord Corp.
Photographic printing plate	Ethylene	W. Germany 2,203,732	1973	Kalle A.G.
Coatings	Isobutylene	W. Germany 2,235,357	1973	Kuraray
Hair spray resins	Ethylene	W. Germany 2,239,698	1973	Monsanto

Powder coatings	Propylene	W. Germany 2,240,027	1973	Cabot Corp.
Phosphate coating modifiers	Ethylene	W. Germany 2,248,867	1973	Dulux Australia
Photocrosslinkable resins, films	1-Hexene	W. Germany 2,306,531	1973	3M
dielectric barrier				
Glass bottle coatings	Ethylene	W. Germany 2,309,777	1973	Dart Ind.
Coatings	Dicyclopentadiene	Japan 11,236	1973	Toho Chemical
Water-soluble resins	Isobutylene	Japan 20,931	1973	Kuraray
Metal coatings	Butadiene	Japan 43,186	1973	Nippon Soda
Enamels, metal coatings	Butadiene	Japan 61,534	1973	Nippon Soda
Coatings	Isobutylene	Japan 61,545	1973	Kuraray
Coatings	Vinylcyclohexane, vinylcyclohexene	U.S.S.R. 370,215	1973	Institute of Petrochemical Synthesis
Coatings	C <sub>5</sub> -C <sub>12</sub> branched $\alpha$ -olefins	U.S.S.R. 384,836	1973	Institute of Petrochemical Synthesis
Coatings	C <sub>5</sub> -C <sub>12</sub> branched $\alpha$ -olefins	U.S.S.R. 403,693	1973	Institute of Petrochemical Synthesis
Corrosion-resistant coating—glass, metals	Ethylene	United States 3,810,276	1974	Texaco, Inc.
Diffusion transfer coating photographic films	Ethylene	United States 3,819,371	1974	Polaroid
Sunscreen body resins	Ethylene	United States 3,821,363	1974	A. S. Black
Photographic film modifier	Ethylene	United States 3,833,370	1974	Polaroid
Coatings	Isobutene	United States 3,845,383	1974	Kuraray
Wax paper coatings	Ethylene	France 2,189,476	1974	Ethylene-Plastique
Photoresist coatings	Ethylene	W. Germany 2,310,307	1974	Rolle A.G.
Coatings	Butenes	Japan 19,110	1974	Kuraray
Electrophoretic resins	Butadiene	Japan 20,613	1974	Dai Nippon Tonyo
Oxidants carrier for photographic films	Ethylene	United States 3,868,252	1975	Eastman Kodak
Metal coating primers	Ethylene	Australia 463,181	1975	Dulux Australia
Binder, dispersant—photographic silver halide emulsions	Ethylene	Belgium 849,122	1975	GAF
Coatings	Cyclopentene	W. Germany 2,343,093	1975	Bayer
Coatings	Ethylene	W. Germany 2,403,516	1975	VEB Leunawerke



Table A.3 (cont.)

Applications	Olefins	Patent	Year	Assignee
Deicing coatings	Ethylene	W. Germany 2,423,893	1975	Chemische Werke Huels
Polyelectrolyte films	Isobutylene	W. Germany 2,429,236	1975	Dow Chemical
Polyolefin coatings	Ethylene	W. Germany 2,455,443	1975	Mitsui Petrochemical Ind.
Transfer coating resins	Ethylene	W. Germany 2,457,623	1975	Mecanorma Export A.G.
Photocrosslinkable resins	Ethylene	Japan 20,215	1975	Kansai Paint
Coatings	Diisobutylene	Japan 33,225	1975	Kao Soap
Photographic film coatings	C <sub>3</sub> -C <sub>10</sub> $\alpha$ -olefins and branched olefins	Japan 36,021	1975	Fuji Photo Film
Primer coating—inorganic materials	Isoprene	Japan 40,637	1975	Kuraray
Photosensitive resins	Isobutylene	Japan 47,888	1975	Kansai Paint
Coatings	Ethylene	Japan 115,289	1975	VEB Leuna Werke
Adhesives, coatings	Isobutylene	Japan 148,503	1975	Sumitomo Chemical
Thermoset emulsion	Isobutene	Japan 149,777	1975	Kuraray
Wood coatings	Isobutylene	Japan 160,332	1975	Kuraray
Wood coatings	Isobutylene	Japan 160,333	1975	Kuraray
Dye diffusion coatings	Ethylene	France 2,290,698	1976	Eastman Kodak
Hair dye carrier resin	Ethylene	W. Germany 1,617,707	1977	Oreal S.A.
Aqueous paint resins	Ethylene	Japan 936	1977	Kuraray
Aqueous paint resins	Ethylene	Japan 937	1977	Kuraray
Photocrosslinkable coatings	Ethylene	Japan 63,984	1977	Kansai Paint
Photopolymerizable resin systems	Isobutylene	Japan 68,283	1977	Kansai Paint
Coatings	C <sub>2</sub> -C <sub>8</sub> $\alpha$ -olefins	Japan 82,687	1977	Kuraray
Coatings, adhesives	Ethylene	Japan 132,091	1977	Kansai Paint
Photoactive printing plate resins	Isobutene	Japan 136,290	1977	Kansai Paint
Reversible resins coatings, dyeing aids, tackifying agent	Butadiene	Netherlands 4,408	1977	Nippon Oil
Reversible resins coatings, dyeing aids, tackifying resins	Butadiene, isoprene, piperylene	United States 4,072,646	1978	Nippon Oil
Release agents, adhesives	Ethylene	United States 4,076,666	1978	Formica Corp.

Photocrosslinkable resins	Ethylene, propylene, butenes, etc.	United States 4,092,172	1978	Kansai Paint
Thermal recording material	Isobutylene	Japan 1,040	1978	Richoh
Moldings, coatings, and adhesives	Ethylene	Japan 1,519	1978	Toyo Soda
Coatings, adhesives	Ethylene, propylene, isobutylene, pentene-1	Japan 20,554	1978	Hitachi Chemical
Coatings, adhesives	Ethylene, propylene, isobutylene pentene-1	Japan 20,555	1978	Hitachi Chemical
Crosslinked PVA compositions	C <sub>2</sub> -C <sub>8</sub> $\alpha$ -olefins	Japan 25,692	1978	Kasei Chemical
Photoconductive resins	Ethylene	Japan 69,038	1978	Fujikura Kasei
Anionic polymeric resist agents	Butadiene, isoprene	Japan 70,184	1978	Nippon Oil
Derivative as epoxy resin hardeners	$\alpha$ -Olefins	Japan 90,397	1978	Kansai Paint
Release coatings	1-Octadecene	United States 4,118,541	1979	Formica Corp.
Photocurable resins	Isobutylene	United States 4,167,415	1979	Kansai Paint
Crosslinked, removable glass coatings	Ethylene	W. Germany 1,596,889	1979	Libby-Owens-Ford
Hot-Melt traffic marker coatings	C <sub>&gt;10</sub> $\alpha$ -olefins	Japan 36,344(5)	1979	Nippon Zeon
High-solids coatings	Isobutylene	Japan 37,133	1979	Kuraray
Calcium carbonate powder coatings	Isobutylene	Japan 45,699	1979	Shiraishi Kogyo
Water and chemical proofing coatings	Isobutylene	Japan 93,687	1979	Ishikawa Sangyo
Coatings	Isobutylene	Japan 94,525	1979	Kasei Chemical
Flame spray coatings for metals	Ethylene	Japan 155,242	1979	Nippon Petrochemicals
Developer compositions for electro-static images	Ethylene	Europe 10,801	1980	AGFA-Gevaert A.G.
Heat-sensitive recording paper coatings	Isobutylene	Japan 7,160	1980	Tomoe-gawa Paper Mfg.
Waterproofing copolymer emulsions	Ethylene, propylene	Japan 52,374	1980	Toa Gosei Chemical
Aqueous emulsion coatings for steel	C <sub>&gt;30</sub> $\alpha$ -olefins	Japan 73,764	1980	Nippon Oil
Steel corrosion inhibitor	C <sub>20-30</sub> $\alpha$ -olefins	Japan 85,679	1980	Mitsubishi Chemical
Coatings	Isobutylene	Japan 140,734	1980	Matsushita Electric
Epoxy resin hardener	1-Hexene	U.S.S.R. 711,631	1980	A.S. Nikadambaer
Polyol crosslinked	Ethylene	Japan 4,313	1981	Ethylene Plastique
Crosslinked coatings	Ethylene	W. Germany 2,214,450	1981	Ethylene Plastique

Table A.3 (cont.)

Applications	Olefins	Patent	Year	Assignee
COMPOSITES				
Foundry sand binder	Ethylene	United States 2,817,128	1957	Monsanto
Foundry mold binders	Ethylene	United States 3,005,245	1961	Monsanto
Polyelectrolytes for dental preparations	Ethylene	United States 3,429,963	1969	Colgate-Palmolive
Binder-Nitric acid blasting caps	Ethylene	United States 3,454,438	1969	American Cyanamid
Gypsum binder	Isobutene	Japan 39,581	1973	Kuraray
Gypsum binder	Isobutene	Japan 40,892	1973	Kuraray
Composites	Ethylene	U.S.S.R. 406,847	1973	Lensovet Technical Institute
Refractory (Al <sub>2</sub> O <sub>3</sub> ) binder resin	Isobutylene	Japan 103,606	1974	Kuraray
Refractory (Al <sub>2</sub> O <sub>3</sub> ) binder	Isobutene	Japan 102,606	1975	Kuraray
Concrete additives	Pentene, hexene, cycloalkenes, norbornene	W. Germany 2,532,050	1976	Nippon Zeon
Gypsum binder	Isoprene, butadiene	Japan 60,217	1976	T. Yamada
Inorganic composite binder	Propylene, butadiene	Japan 5,247	1978	Japan Synthetic Rubber
Sand mold resins	$\alpha$ -Olefins	Japan 5,133	1980	Hitachi Ltd.
CONTROLLED RELEASE POLYMERS				
Fertilizer carrier or binder	Isobutylene	United States 2,703,276	1955	Monsanto
Medicinal coatings	Ethylene	Belgium 622,793	1963	Eli Lilly
Antidiarrhea preparations	Ethylene	Belgium 644,140	1964	Eli Lilly
Microscopic capsule coatings	Ethylene	United States 3,190,837	1965	National Cash Register
Antidiarrhea tablets, capsules	C <sub>2</sub> -C <sub>5</sub> $\alpha$ -olefins	United States 3,224,941	1965	Eli Lilly Co.
Capsule coatings	Ethylene	France 1,524,629	1968	National Cash Register
Microencapsulation coatings	Ethylene	South Africa 5,745	1968	National Cash Register
Microencapsulating resins	Ethylene	W. Germany 1,817,316	1969	Pilot Pen
Hair spray resins, medicinal coatings	Ethylene	W. Germany 1,930,009	1969	Monsanto
Capsule coatings	Ethylene	South Africa 8,348	1969	National Cash Register



Microcapsule coatings	Ethylene	W. Germany 1,900,865	1970	Farbenfabriken Bayer
Diarrhea treatment agent for animals	Ethylene	South Africa 126	1970	Monsanto
Blood cholesterol reduction agent	1-Octadecene	South Africa 127	1970	Monsanto
Capsule coatings	Ethylene	United States 3,594,327	1971	National Cash Register
Placebo tablet coatings	Ethylene	Britain 1,233,468	1971	Imperial Chemical
Animal cholesterol reduction tablets	1-Octadecene, ethylene	France 2,084,603	1971	Monsanto
Blood cholesterol reducer	1-Octadecene	W. Germany 2,000,567	1971	Monsanto
Animal diarrhea control agents	Isobutylene, 1-octadecene	Britain 1,260,451	1972	Monsanto
Microencapsulated iron	Ethylene	France 2,107,697	1972	Merck and Co.
Hydrocortison slow-release carrier	Ethylene	W. Germany 2,363,963	1974	Alza Corp.
Opthalmic medicinal slow-release carrier	Ethylene	United States 3,914,402	1975	Alza Corp.
Animal feed additive—blood cholesterol reduction	1-Octadecene	United States 3,923,972	1975	Monsanto
Improved microcapsule compositions	Ethylene	Japan 15,660	1980	Mitsubishi Paper Mills
Microcapsule coatings	Isobutylene	Japan 75,736	1980	Kuraray Co.
Cholesterol reduction agent	C <sub>10-30</sub> $\alpha$ -olefins	Netherlands 166,189	1981	Monsanto Co.

COSMETIC ADDITIVES

Cosmetics emulsifier	1-Octadecene	Belgium 707,486	1968	Oreal S.A.
Cosmetics emulsifier	1-Hexadecene	Belgium 707,487	1968	Oreal S.A.
Cosmetics dispersant	1-Octadecene	W. Germany 1,813,326	1969	Oreal S.A.
Cosmetic coatings	Ethylene	United States 3,523,998	1970	Plough, Inc.
Cosmetics dispersant, cosmetics emollient, gels	Ethylene	United States 3,609,192	1971	Paris Cosmetics
Thickening agent, cosmetics dispersant	Ethylene	W. Germany 2,113,213	1971	GAF

Table A.3 (cont.)

Applications	Olefins	Patent	Year	Assignee
<i>DETERGENT ADDITIVES</i>				
Binder-detergent beads	Ethylene	United States 3,380,922	1968	Purex Corp.
Textile detergent builder	Butadiene	W. Germany 1,920,850	1969	Borg-Warner
Detergent	Ethylene, dicyclopentadiene	W. Germany 1,816,510	1970	Farbenwerke Hoeschst
Detergent builder stabilizer	Ethylene	W. Germany 1,959,272	1970	Procter & Gamble
Detergent builder dispersant	Ethylene	W. Germany 1,961,959	1970	Economics Laboratory
Emulsion detergents	Ethylene	United States 3,574,122	1971	Lever Brothers
Liquid detergent additive	Ethylene	United States 3,629,125	1971	Lever Brothers
Liquid detergent additive	Ethylene	W. Germany 2,062,482	1971	Procter & Gamble
Enzyme binder resins, detergent additive	Ethylene	Britain 1,286,095	1972	Fuji Photo Film
Detergent builder	Ethylene propylene	W. Germany 2,056,813	1972	Chemische Werke Huels
Detergent modifier	Ethylene	United States 3,717,589	1973	Monsanto
Detergent builder enzyme carrier	Ethylene	France 2,160,661	1973	Unilever N.V.
Detergent additives, soil redeposition inhibitors	Ethylene, propylene	W. Germany 2,165,802	1973	Henkel & Cie
Thickeners, dispersants, adhesives, detergent additives	Dicyclopentadiene, indene, alkenylnorbornenes	W. Germany 2,237,525	1973	Snam Progetti S.p.A.
Detergent builders	Cyclopentene, ethylene, propylene, butenes	W. Germany 2,238,275	1973	Hitachi Chemical
Spray dried detergents	Ethylene	W. Germany 2,264,302	1973	Unilever N.V.
Detergent modifier	Ethylene, propylene, isobutene	W. Germany 2,432,561	1973	Toyo Soda
Detergent stabilizer	Ethylene	W. Germany 2,300,654	1974	Chemische Werke Huels
Detergent builder, water softening agent	Tetrahydrophthalic anhydride	Britain 1,382,985	1975	Imperial Chemical
Laundry detergent additives	Isobutylene	Japan 118,096	1975	Kuraray

DISPERSANTS/EMULSIFIERS

Dye carrier—photographic emul- sions	Ethylene	United States 2,389,575	1945	DuPont
Dye carrier—photographic emul- sions	Ethylene	Britain 569,646	1945	DuPont
Detergent modifiers	Ethylene, propylene, isobutylene	Britain 872,530	1957	Monsanto
Dispersant for PVC production	Ethylene	United States 2,823,200	1958	Monsanto
Emulsifiers for PVC production	Ethylene	United States 2,824,862	1958	Monsanto
Emulsifiers for PVC production	Ethylene	United States 2,917,396	1959	Monsanto
Dispersant for PVC production	Ethylene	United States 2,917,494	1959	Monsanto
Pigment binder, carbon black dis- persant	Diisobutylene	United States 2,930,775	1960	Rohm & Haas
Drilling mud additives, inorganic pigment dispersants	Ethylene, propylene, isobutylene	United States 2,938,016	1960	Monsanto
Photographic emulsion stabilizer	Ethylene	United States 2,957,767	1960	Monsanto
Dispersant for PVC production	Ethylene	United States 2,957,857	1960	Monsanto
Dispersants for PVC production	Ethylene	United States 2,979,487	1961	Monsanto
Ester derivatives—photographic sol- ution stabilizers	Ethylene	United States 2,980,534	1961	Monsanto
Pigment dispersant	Diisobutylene	W. Germany 1,119,434	1961	Rohm & Haas, G.m.b.H.
Liquid detergent stabilizer	Ethylene	United States 3,060,124	1962	Monsanto
Coatings, surfactants, adhesives	Butadiene	Belgium 617,612	1962	Shell International
Photographic emulsion stabilizer	Ethylene	W. Germany 1,136,110	1962	Gevaert Photo Producten
Organic pigment dispersant	Ethylene	United States 3,200,000	1965	Monsanto
Dispersants	Diisobutylene	Belgium 658,993	1965	Kao Soap
Liquid detergent	Ethylene	Belgium 662,984	1965	Unilever N.V.
Liquid detergent additives	Ethylene	United States 3,235,505	1966	Monsanto
Organic pigment dispersant	Ethylene	United States 3,236,797	1966	Monsanto
Organic pigment dispersant	Ethylene	United States 3,249,455	1966	Monsanto
Polyolefins, emulsifiers	Ethylene	United States 3,258,440	1966	Phillips Petroleum
Dispersant-latex coating stabilizer	Ethylene, isobutylene	United States 3,262,898	1966	Monsanto
Organic pigment dispersant	Ethylene	United States 3,322,713	1967	Monsanto
Organic pigment dispersant	Isobutylene, ethylene	France 1,506,860	1967	Farbenfabriken Bayer A.G.
Pigment dispersant	Hexene-1	Netherlands 14,526	1967	Gulf Research



Table A.3 (cont.)

Applications	Olefins	Patent	Year	Assignee
Cosmetics emulsifier	1-Octadecene	Belgium 707,486	1968	Oreal S.A.
Cosmetics emulsifier	1-Hexadecene	Belgium 707,487	1968	Oreal S.A.
Protective colloid	Ethylene	E. Germany 62,915	1968	H. Pobloth
Platex emulsifier	Ethylene	France 1,511,183	1968	Monsanto
Petroleum dewaxing agent	1,5-Cyclooctadiene	United States 3,449,236	1969	Esso Research
Silver halide dispersant photo-graphic films	Ethylene	W. Germany 1,904,147	1969	Eastman Kodak
Foam stabilizer washing solutions	Butadiene	W. Germany 1,919,723	1969	Borg-Warner
Dispersants	Butadiene, isoprene	W. Germany 1,919,917	1969	Borg-Warner
Dispersant	Isoprene	W. Germany 1,919,918	1969	Borg-Warner
Dispersant	Butadiene	W. Germany 1,919,919	1969	Borg-Warner
Dispersant—silver halide emulsions, photographic films	Ethylene	France 1,586,036	1970	Eastman Kodak
Dispersant textile finishes	Ethylene, isobutylene	W. Germany 1,904,233	1970	Farbenfabriken Bayer A.G.
Dye dispersant—plastics	Isobutylene	W. Germany 1,930,217	1970	Farbenfabriken Bayer A.G.
Detergent builder stabilizer	Ethylene	W. Germany 1,959,272	1970	Procter and Gamble
Detergent builder dispersant	Ethylene	W. Germany 1,961,959	1970	Economics Laboratory
Dispersants	C <sub>30</sub> $\alpha$ -Olefins	United States 3,553,177	1971	Gulf Research
Dispersants	C <sub>20</sub> -C <sub>30</sub> $\alpha$ -olefins	United States 3,560,455	1971	Gulf Research
Dispersants	1-Octadecene, 1-hexadecene	United States 3,560,456	1971	Gulf Research
Dispersants	1-Dodecene, 1-tetradecene	United States 3,560,457	1971	Gulf Research
Dispersant	Butadiene	United States 3,575,942	1971	Borg-Warner
CaCO <sub>3</sub> dispersant binder for paper coatings	Ethylene	United States 3,597,251	1971	Wyandotte Chemical
Photographic emulsion stabilizer	Ethylene	United States 3,598,599	1971	Eastman Kodak
Photographic film antifoggers	Ethylene	United States 3,598,600	1971	Eastman Kodak
Cosmetics dispersant, cosmetics emollient gels	Ethylene	United States 3,609,192	1971	Paris Cosmetics
Silver halide peptizer, photographic films	Ethylene	United States 3,615,624	1971	Eastman Kodak

Dispersant for photographic films	Ethylene	W. Germany 1,937,374	1971	Agfa–Gevaert
Thickeners, dispersants	5-Norbornen-2-yl methyl	W. Germany 1,948,198	1971	Henkel & Cie
Detergent additive	Butadiene	W. Germany 2,125,461	1971	Borg–Warner
Scale inhibitor, cleaning agent	Ethylene	United States 3,679,592	1972	Monsanto
Foam stabilizers	Butadiene	United States 3,681,253	1972	Borg–Warner
Cleaning agent additive	Ethylene	United States 3,700,599	1972	Economics Laboratory
Rubber dispersant	Isobutene	W. Germany 2,039,494	1972	Farbenfabriken Bayer A.G.
Suspending agent—PVC preparation	C <sub>6</sub> –C <sub>20</sub> $\alpha$ -olefins	W. Germany 2,225,221	1972	Gulf Oil
Dispersants	1-Hexene, 1-decene, 1-octadecene	United States 3,729,451	1973	Gulf Research
Thickeners, dispersants, adhesives, detergent additives	Dicyclopentadiene, indene, alkenyl-norbornenes	W. Germany 2,237,525	1973	Snam Progetti S.p.A.
Laundry detergent builder	Ethylene	W. Germany 2,240,309	1973	Unilever N.V.
Hair shampoo resins	Ethylene	W. Germany 2,310,283	1973	Unilever N.V.
Dispersant	Isoprene	W. Germany 2,316,112	1973	Borg–Warner
Adhesives, pigment dispersant, detergent additives	1-Butene	Japan 42,094	1973	Kuraray
Fiber delustering agent, TiO <sub>2</sub> dispersant	Diisobutylene	United States 3,793,277	1974	Celanese
SBR emulsifier	Dicyclopentadiene	Japan 2,194	1974	Toho Chemical
SBR emulsifier	Dicyclopentadiene	Japan 31,628	1974	Arakawa Forest Chemicals Ind.
Binder dispersant—photographic silver halide emulsions	Ethylene	Belgium 849,122	1975	GAF
Dispersant—fluidizing agent	1,5-Cyclooctadiene	France 2,247,277	1975	Gulf Research
Latex emulsifiers	Ethylene	France 2,252,358	1975	Dow Chemical
Shampoo foam stabilizers	Ethylene, propylene	W. Germany 2,347,553	1975	Chemische Werke Huels
Dispersants coatings	Isoprene, pentenes, methyl butenes, <i>cis</i> -piperylene, <i>trans</i> -piperylene, cyclopentadiene	W. Germany 2,504,378	1975	Neste Oy
Anionic rubber surfactant	Diisobutylene	Japan 8,096	1975	Japan Synthetic Rubber
Protective colloid	Isobutylene	Japan 55,648	1975	Konishi Gisuke
SBR emulsifier, wood adhesives	Isobutylene	Japan 126,039	1975	Nippon Oils and Fats
PVA dispersant	Isobutene	Japan 146,581	1975	Kuraray
Nonmigratory resin emulsifiers	Ethylene, propylene, butenes	United States 3,932,333	1976	Monsanto

Table A.3 (cont.)

Applications	Olefins	Patent	Year	Assignee
Dispersant	Ethylene	United States 4,025,482	1977	Monsanto
Adhesives, coatings, dispersant, textile and paper sizing	Dicyclopentadiene	W. Germany 2,656,830	1977	Borg-Warner
Fire extinguisher additives	Butadiene	Japan 99,699	1977	Nippon Oil
Water-soluble quenching agents for metals	Butadiene, isoprene	United States 4,090,891	1978	Nippon Oil
Dispersants, stabilizers	Butadiene, isoprene	United States 4,102,667	1978	Lindau Chemicals
Emulsion paint thickener	Diisobutylene	Britain 1,511,652	1978	Albright & Wilson Ltd.
Magnetic particle dispersant	$\alpha$ -Olefins	Canada 1,043,638	1978	Fuji Photo Film
Reversible resins, adhesives, thickeners, fire extinguisher additive	Butadiene, isoprene	Japan 20,075	1978	Nippon Oil
Reversible resins, adhesives, fire extinguisher additive	Butadiene, isoprene	Japan 20,552	1978	Nippon Oil
Solid-liquid phase reversible systems	Conjugated dienes	United States 4,170,583	1979	Nippon Oil
Hydrocolloid gelling agent	Isobutylene	United States 4,172,055	1979	Celanese
Coating dispersions	Ethylene	United States 4,173,669	1979	Asahi Dow
Paint pigment dispersants	Diisobutylene	Australia 499,791	1979	Albright and Wilson
Talc dispersion aid	Diisobutylene	Britain 2,019,822	1979	Albright and Wilson
Dispersing agents	Ethylene	W. Germany 2,841,562	1979	Rohner A.G.
Phase reversible systems	Butadiene	Japan 13,474	1979	Nippon Oil
Nonaqueous coating surfactants	Diisobutylene	Japan 34,011	1979	Kao Soap
Polymer dispersions agent	$>C_{20}$ $\alpha$ -Olefins	Japan 108,892	1979	Nippon Zeon
Fire extinguisher compositions	Isobutylene	Netherlands 124,600	1979	Nippon Oil
Aqueous $I_2$ complex compositions	$C_{2-3}$ $\alpha$ -Olefins	W. Germany 2,827,827	1980	BASF A.G.
Fire extinguisher additive	Butadiene	Japan 29,323	1980	Nippon Oil
Dispersant and wetting material for image recording materials	Diisobutylene	Japan 53,595	1980	Daishowa Giken Kogy
Oil-based paste polishes	$C_{30-50}$ $\alpha$ -olefins	Japan 58,274	1980	Nippon Oil



Silver halide—photographic emulsions	C <sub>4</sub> or higher $\alpha$ -olefins	Japan 69,139	1980	Mitsubishi Paper Mills
Washing agent additive for vacuum casting molds	Isobutylene	Japan 75,847	1980	Hitachi KK
Corrosion inhibitors	C <sub>30-60</sub> $\alpha$ -olefins	Japan 85,679	1980	Mitsubishi Chemical
Dispersant for aqueous dye systems	Isobutylene	Japan 104,360	1980	Nippon Kagaku
Crosslinked material as dispersant	Ethylene	U.S.S.R. 712,415	1980	—
Emulsion pdymerization dispersant	Dicyclopentadiene	Japan 33,302	1981	Kanegafuchi Chemical

ELASTOMERS

Elastomers	Butadiene	Britain 1,141,558	1969	Shell
Elastomers	Dipentene	Britain 1,184,764	1970	Cassella Farbwerke
Rubber additive	Pentene, isoprene	Britain 1,204,730	1970	Shell
Thermoplastic elastomers	Isoprene, butadiene	W. Germany 1,905,423	1979	Shell

ENZYME/MEDICINAL CARRIER

Enzyme binder resin	Ethylene	W. Germany 1,943,490	1970	Monsanto
Enzyme binder resin	Ethylene	W. Germany 1,944,369	1970	Yeda Research
Enzyme binder resin	Ethylene	W. Germany 1,945,680	1970	Monsanto
Enzyme binder resin	Ethylene	W. Germany 1,945,748	1970	Monsanto
Enzyme binder resins	Ethylene	W. Germany 1,948,177	1970	Monsanto
Enzyme binder resins	Ethylene	W. Germany 1,948,273	1970	Monsanto
Polymeric enzyme mouthwash	Ethylene	W. Germany 1,948,298	1970	Monsanto
Polymeric enzyme chillproofing agent	Ethylene	United States 3,597,219	1971	Monsanto
Enzyme carrier, beer clarifier	Ethylene	United States 3,597,220	1971	Monsanto
Beer clarifier agent	Ethylene, isobutylene, 2-methylpene-1	United States 3,597,221	1971	Monsanto
Enzyme binder resin	Ethylene	United States 3,627,640	1971	Yeda Research
Enzyme binder resins	Ethylene	W. Germany 2,106,215	1971	Monsanto

Table A.3 (cont.)

Applications	Olefins	Patent	Year	Assignee
Enzyme binder resins	Ethylene	United States 3,650,900	1972	Yeda Research
Virus binder resins	C <sub>2</sub> -C <sub>12</sub> $\alpha$ -olefins	United States 3,651,213	1972	Monsanto
Polyampholytic virus collector	Ethylene	United States 3,655,509	1972	Monsanto
Hormone carrier	Ethylene	United States 3,679,653	1972	Monsanto
Enzyme binder resins, detergent additive	Ethylene	Britain 1,286,095	1972	Fuji Photo Film
Plasminogens absorption resins	Propylene	W. Germany 2,057,401	1972	Behringwerke A.G.
Polypeptide carrier	Isobutylene	United States 3,737,412	1973	Monsanto
Detergent builder enzyme carrier	Ethylene	France 2,160,661	1973	Unilever N.V.
Biologically active protein carrier	Ethylene	W. Germany 2,420,747	1974	Yeda Research
Protein carrier	Propylene	W. Germany 2,363,854	1975	Behringwerke A.G.
Water-soluble protein carrier	Ethylene	W. Germany 2,530,247	1976	Yeda Research
EPOXY RESIN HARDENER				
Dispersant, thickener, textile and paper sizing, epoxy resin hardener	Cyclopentadiene, methylcyclopentadiene	W. Germany 2,656,871	1977	Borg-Warner
FIBERS/FABRICS				
Textile finishes, sizing agents	Ethylene	W. Germany 902,367	1954	Dynamit Akt.
Textile sizing agent, paper sizing resins	Diisobutylene	United States 2,725,367	1955	Rohm & Haas
Sizing for nylon fiber	Ethylene	W. Germany 1,016,228	1957	Monsanto
Nylon sizing agent	Ethylene, propylene	United States 2,854,357	1958	Monsanto
Nylon sizing resins	Propylene	Britain 871,589	1958	Monsanto
Polyester sizing agent	Ethylene	United States 2,992,736	1959	Monsanto
Water evaporation dyes	Isobutylene, ethylene	United States 3,099,630	1963	Monsanto
Textile printing pastes	Ethylene	Belgium 634,059	1963	Interchemical Corp.
Textile printing resins	Ethylene	United States 3,138,567	1964	Interchemical Corp.

Thickening agent, textile printing inks	Ethylene	United States 3,165,486	1965	Monsanto
Textile printing extender	Ethylene	France 1,439,032	1966	Geigy A.G.
Wool textile creasing agent	Ethylene	Netherlands 2,090	1966	Oreal S.A.
Thickeners—textile printing pastes	Ethylene	United States 3,393,168	1968	Monsanto
Fiber modifier	Ethylene	United States 3,425,969	1969	J. J. Press
Dispersant textile finishes	Ethylene, isobutylene	W. Germany 1,904,233	1970	Farbenfabriken Bayer, A.G.
Soil release—creaseproofing coatings	Butadiene, isoprene	W. Germany 2,028,669	1971	Borg-Warner
Polyolefin dye improver	Ethylene	W. Germany 2,060,330	1971	Ethylene-Plastique
Polyester fiber sizing	Diisobutylene	W. Germany 2,118,699	1971	Kao Soap
Fabric soil release coatings	Butadiene	United States 3,684,568	1972	Borg-Warner
Antistatic coatings—fibers and plastics	Ethylene	Japan 50,781	1972	Toyo Spinning
Gelatin coacervate fibers	Ethylene	United States 3,757,004	1973	Stanford Research
Yarn (textile) cohesion coating	Diisobutylene	W. Germany 2,317,294	1973	Kao Soap
Fiber lubricant	Diisobutylene	Japan 41,098	1973	Kao Soap
Olefin fiber coatings	Tetradecene	Japan 47,619	1973	Gulf Research
Rayon fiber coatings	Isobutylene	Japan 98,120	1973	Kuraray
Rayon fiber modifier	Isobutylene	Japan 99,416	1973	Kuraray
Fiber delustering agent, TiO <sub>2</sub> dispersant	Diisobutylene	United States 3,793,277	1974	Celanese
Glass fiber sizing agents	Butadiene	United States 3,816,235	1974	Borg-Warner
Glass fiber coatings	1,3-Butadiene	W. Germany 2,341,474	1974	Owens-Corning
Paper and textile coatings	Isobutene	Japan 11,853	1974	Kuraray
Textile printing thickeners	Ethylene	United States 3,887,509	1975	Inmont Corp.
Textile soil release coatings	Ethylene	United States 3,897,206	1975	Bibb Co.
Cotton fabric sizing agent	Isobutene	Japan 101,685	1975	Kuraray
Textile sizing resins	Ethylene	W. Germany 1,928,868	1976	Chemische Werke Huels
Textile soil release coatings	Ethylene	United States 4,038,027	1977	Bibb Co.
Water-repellent finishes	Ethylene	United States 4,070,152	1977	Ciba-Geigy
Thickener, textile printing resin	Ethylene	Britain 1,479,114	1977	Monsanto
Thickener, stabilizer, textile and paper coating	Butadiene	W. Germany 1,795,660	1977	Borg-Warner



Table A.3 (cont.)

Applications	Olefins	Patent	Year	Assignee
Reversible resins, dyeing aid, tackifying agent	Isoprene	Japan 91,053	1977	Nippon Oil
Wood, glass, metal, leather and textile coatings	Isobutylene	Japan 35,736	1978	Union Paint
Pastes for printing textiles	Butadiene	Japan 160,878	1979	Nippon Oil
Imidized materials for sizing agents	C <sub>2-6</sub> $\alpha$ -olefins	E. Germany 140,147	1980	VEB Leuna-Werke
FILMS				
Molding compounds, coatings, packaging films	Diisobutylene, 2-methyl-1-heptene	United States 2,373,067	1945	Standard Oil
Orientated films	Isobutylene	Netherlands 11,809	1960	Imperial Chemical
Gelatin hardener, photographic films	Ethylene	W. Germany 1,149,517	1963	Henkel & Cie
Epoxy resin curative	1,5-Cyclooctadiene	United States 3,261,815	1966	PPG
Photographic films	Ethylene	United States 3,296,155	1967	Eastman Kodak
Gelatin hardeners	Ethylene	United States 3,306,750	1967	Eastman Kodak
Image receiving coatings, photographic films	Ethylene	United States 3,376,137	1968	Polaroid
Silver halide dispersant photographic films	Ethylene	W. Germany 1,904,147	1969	Eastman Kodak
Dispersant—silver halide emulsions, photographic films	Ethylene	France 1,586,036	1970	Eastman Kodak
Transparent packaging materials	Ethylene, isobutylene	W. Germany 1,806,269	1970	Farbenfabriken Bayer A.G.
Free films, coatings	Butadiene, isoprene, chloroprene, piperylene, 2,3-dimethylbutadiene, 2,4-hexadiene	Britain 1,238,934	1971	Borg-Warner
Printing films	Ethylene	United States 4,202,923	1980	Hoechst A.G.

Photographic films coating	Ethylene	Japan 96,946	1980	Mitsubishi Paper Mills
Antistatic coatings—photographic films	Isobutylene	U.S.S.R. 720,411	1981	Chem. Photo
Photographic colour diffuser	Ethylene	United States 4,267,262	1981	Fuji Photo
ION-EXCHANGE RESINS				
Sulfonated cation-exchange resins	Dicyclopentadiene	United States 2,731,426	1956	Rohm & Haas
Ion-exchange resins	Dimethallyl	United States 2,955,994	1960	Esso Research
Thickener, protective colloid, ion-exchange resin	Propylene, isobutylene	France 1,466,860	1967	Oesterreichische Stickstoffwerke
Separation media resin	Ethylene	W. Germany 2,418,708	1974	Miles Laboratories
Rennin isolation resin	Ethylene	W. Germany 2,419,232	1974	Miles Laboratories
Separation media resin	Ethylene	U.S.S.R. 494,394	1975	Inst. Heteroorganic Compounds
Polyelectrolyte for blood separations	Ethylene	Brazil 4,728	1979	Monsanto
Chromatography carrier for disulphide exchange reactions	Ethylene	U.S.S.R. 687,081	1979	—
Agent to remove mercaptan from blood	Ethylene	United States 4,252,645	1981	Snam Progetti SPA

LAMINATES

Thermosetting resins	Ethylene	United States 2,519,764	1950	DuPont
Varnish and impregnant resins	Indene	W. Germany 1,110,416	1961	Bergwerksverband
Paper laminates	Ethylene	W. Germany 1,147,382	1963	Henkel & Cie
Molding, films, and laminating resins	1,4-Pentadiene	United States 3,320,216	1967	Peninsular Chem Research
Laminates—polyolefins	Ethylene	United States 3,340,091	1967	Morton Int.
Thermosetting resins	1-Hexene	United States 3,441,543	1969	Gulf Research
Laminates	Ethylene	Britain 1,161,097	1969	Dow Chemical
Al foil laminates	Ethylene	W. Germany 2,203,388	1972	Ethylene-Plastique
Moldings—laminates	Ethylene	Japan 34,839	1972	Asahi Chemical

Table A.3 (cont.)

Applications	Olefins	Patent	Year	Assignee
Laminates	3a,4,5,6,7,7a-Hexahydro-methanoindene	Japan 44,028	1972	Hitachi Chemical
Glass fiber moldings	1-Hexene	United States 3,717,557	1973	Gulf Oil
Heat-resistant resin laminates, adhesives	Butadiene	Japan 37,940	1974	Tokyo Shibaura Electric
Laminates	Ethylene	Japan 77,485	1975	Mitsui Petrochemical
Decorative laminate release agent	1-Octadecene	Europe 11,966	1980	Scott Paper
<i>LEATHER MODIFIERS</i>				
Leather coatings	Ethylene	W. Germany 2,101,160	1971	State Research Institute Kozedelny
Synthetic leather	Ethylene	W. Germany 2,101,158	1972	State Research Institute Kozedelny
Leather substitute coatings for leather	Butadiene, chloroprene, isoprene	Japan 20,782	1973	Teijin Ltd.
<i>LITHOGRAPHIC PLATES</i>				
Photosensitive coatings lithographic printing plates	Ethylene	Britain 1,135,082	1968	Algraphy Ltd.
Lithographic printing plate compositions	Ethylene	Japan 7,704	1980	Mitsubishi Paper Mills
Lithographic printing plates	Ethylene	Japan 96,955	1980	Mitsubishi Paper Mills
<i>MEMBRANES</i>				
Sealants for membranes	Ethylene	France 1,534,286	1968	National Cash Register
Osmosis membrane scale prevention agent	Isobutylene	Japan 71,786	1979	Koryu Kogyo



METAL COMPLEXING/SESQUESTERING RESINS

Clay beneficiating agent	Ethylene, propylene, butylene	United States 3,073,805	1963	Monsanto
Metal catalyst supports	Ethylene	W. Germany 2,213,485	1972	Shell
Metal recovery resins for aqueous systems	Ethylene	W. Germany 2,458,066	1975	Mitsubishi Rayon
Ion-exchange resin, metal recovery resins	Isobutene	Japan 78,583	1975	Kuraray
Oxidation-reduction carrier resin	Ethylene, isobutylene	United States 4,065,435	1977	Fuji Photo Film

OIL ADDITIVES

Petroleum additives	Isobutene, ethylene	Dutch 61,145	1948	N.V. de Bataatsche Petroleum Maatschoppij
Pour point depressants, viscosity index improvers	1-Octadecene, tetradecene, 1-dodecene, 1-Decene	United States 2,542,542	1951	Standard Oil
VI index improver	Butadiene monoxide	United States 2,582,708	1952	Standard Oil
Lubricating oils	C <sub>2</sub> -C <sub>24</sub> $\alpha$ -olefins	United States 2,615,845	1952	Standard Oil
Lubricating oils	1-Octene	United States 2,698,316	1954	Socony-Vacuum Oil
Lubricating oil modifier	Octadecene	W. Germany 1,025,626	1958	Esso Research
Oil additives	C <sub>8</sub> -C <sub>18</sub> $\alpha$ -olefins	Britain 852,949	1960	Esso Research
Lube oils	Ethylene	United States 2,992,987	1961	Monsanto
Fuel oils	1-Decene, dodecene, octadecene	United States 3,003,858	1961	Socony Mobil
Jet fuel stabilizer	1-Decene	United States 3,034,876	1962	Socony Mobil
Viscosity control agents	Ethylene	United States 3,083,189	1963	Monsanto
Jet fuel stabilizer	C <sub>2</sub> -C <sub>20</sub> $\alpha$ -olefins	United States 3,115,483	1963	Socony Mobil
Fuel oils	C <sub>15</sub> -C <sub>20</sub> $\alpha$ -olefins	France 1,459,497	1966	Chevron Research
Fuel oils	Ethylene, propylene, isobutylene	United States 3,329,658	1967	Monsanto
Pour point depressants	Bicycloheptene	United States 3,370,047	1968	Union Carbide
Fuel, rust inhibitors	C <sub>15-20</sub> $\alpha$ -olefins	United States 3,382,056	1968	Chevron Research
Diesel fuel detergents	Ethylene	United States 3,413,104	1968	Chevron Research
Oil detergents dispersant	Ethylene, propylene, isobutylene	United States 3,449,250	1969	Monsanto
Diesel fuels	C <sub>8</sub> -C <sub>30</sub> $\alpha$ -olefins	United States 3,471,458	1969	Chevron Research
Lubricant modifiers	Bicyclo[2.2.1] hept-2-ene	United States 3,472,774	1969	Union Carbide

Table A.3 (cont.)

Applications	Olefins	Patent	Year	Assignee
Lubricant modifiers	Ethylene	United States 3,484,504	1969	Universal Oil
Lubricating oils	Ethylene	W. Germany 1,900,838	1969	Esso Research
Lubricating oils	Ethylene	U.S.S.R. 258,586	1969	All-Union Scientific Research Institute
Diesel fuels	Ethylene	United States 3,506,625	1970	Sinclair Research
Oil viscosity reducer	C <sub>22</sub> $\alpha$ -olefins	W. Germany 1,940,944	1970	Mobil Oil
Fuel oil antistatic agent	1-Octadecene	W. Germany 2,005,133	1970	Mobil Oil
Metal working lubricants	Ethylene	United States 3,563,895	1971	Valgene Industrial Research
Lubricating oils	1-Hexene	United States 3,580,893	1971	Gulf Research
Fuel oil antistatic agents	1-Octadecene	W. Germany 2,104,447	1971	Mobil Oil
Lubricating oils	1-Hexene	United States 3,706,703	1972	Gulf Research
Lubricating oils	1-Octene, 1-decene	United States 3,706,704	1972	Gulf Research
Lubricating oil stabilizers	1-Octadecene	United States 3,714,045	1973	Mobil Oil
Lubricating oils	1-Octadecene, 1-tetradecene	United States 3,729,450	1973	Gulf Research
Oil demulsifier	Diisobutylene	United States 3,819,589	1974	Petrolite
Heating oil modifier	Ethylene	W. Germany 2,330,180	1974	Texaco
Lubricating oils, pour point depressants	C <sub>8</sub> -C <sub>10</sub> and C <sub>20</sub> -C <sub>24</sub> $\alpha$ -olefins	Britain 1,525,114	1978	Exxon Research
Lubricating oils	Cyclopentene	W. Germany 2,824,252	1978	Nippon Zeon
Fuel oil modifier	Ethylene	Japan 86,505	1979	Toho Chemical
Fuel oils	C <sub>20-60</sub> $\alpha$ -olefins	Japan 157,106	1979	Mitsubishi-Monanto
Stabilizers for fuel oil-coal mixtures	1-Dodecene	Japan 43,154	1980	Sanyo Chemical

PLASTICS

Polyamides for moldings	Ethylene	United States 2,917,928	1959	Monsanto
Pressure molded objects	Isobutene	Belgium 631,041	1963	Imperial Chemical
Moldings—Coatings	Diisobutylene	Belgium 646,619	1964	Rohm & Haas
Ionomer molded plastics, films	C <sub>1</sub> -C <sub>10</sub> $\alpha$ -olefins	France 1,393,730	1965	DuPont
Castings—coatings	Bicyclo[2.2.1] heptadiene	United States 3,240,763	1966	Dow Chemical

Moldings, films and laminating resins	1,4-Pentadiene	United States 3,320,216	1967	Peninsular Chem Research
Transparent moldings	Isobutene, 2-methyl-1-pentene	Britain 1,087,075	1967	Imperial Chemical
Transparent plastic windshields	Isobutylene, 2-methyl-1-butene	Britain 1,087,297	1967	Imperial Chemical
Potting resins with epoxy resins	C <sub>3</sub> -C <sub>26</sub> $\alpha$ -olefins	United States 3,374,209	1968	Gulf Research
Sizing for celluloseics, potting com-positions	1-Hexene, 1-decene, 1-octadecene	United States 3,459,715	1969	Monsanto
Coatings, moldings	Butadiene	Japan 26,738	1969	Toyo Rayon
Thermoplastics moldings	Ethylene, isobutylene	W. Germany 1,904,652	1970	Farbenfabriken Bayer A.G.
Lactam grafts for moldings	Ethylene	W. Germany 1,905,452	1970	Allied Chemical
Thermoplastics moldings	Isobutylene	W. Germany 1,925,996	1970	Farbenfabriken Bayer
Injection moldings	2-Methylbutene, 2-methyl-1-pentene	United States 3,574,162	1971	Imperial Chemical
Moldings	1-Hexene, propylene, 1-octadecene	United States 3,586,659	1971	Gulf Research
Thermoset moldings	1-Hexene	United States 3,594,354	1971	Gulf Research
Thermoplastics moldings, coatings	4-Vinylcyclohexene	Britain 1,255,838	1971	BP Chemicals
Laminates, moldings	Ethylene	United States 3,632,797	1972	Union Carbide
Molding materials	1-Hexene	United States 3,642,726	1972	Gulf Research
Adhesives, coatings, moldings	1-Methyl-cyclopropene	United States 3,644,301	1972	Shell
Moldings	1-Hexene	W. Germany 2,162,757	1972	Gulf Research
Laminates, moldings	Ethylene	W. Germany 2,214,451	1972	Ethylene-Plastique
Films, moldings	Butadiene	Japan 45,954	1972	Toray Industries, Inc.
Thermosetting sheet moldings	1-Hexene	United States 3,713,927	1973	Gulf Oil
Laminates, moldings	1-Hexene	United States 3,732,337	1973	Gulf Research
Laminates, moldings	1-Hexene	United States 3,741,940	1973	Gulf Research
Organic semiconductor binder	Ethylene	United States 3,754,986	1973	Eastman Kodak
Coatings—moldings	C <sub>4</sub> -C <sub>24</sub> $\alpha$ -olefins	Britain 1,476,765	1973	Exxon Research
Heat moldable plastics	1-Hexene	W. Germany 2,211,410	1973	Gulf Research
Laminates, extruded plastics modifier	Ethylene	Japan 20,280	1974	Mitsui Petrochemical
Antistatic coatings for plastic films	C <sub>3</sub> -C <sub>18</sub> $\alpha$ -olefins	Japan 23,827	1974	Konishiroku Photo
Thermosetting adhesives, moldings	Ethylene, propylene 1-butene	Japan 82,336	1974	Kuraray



Table A.3 (cont.)

Applications	Olefins	Patent	Year	Assignee
Thermoset moldings	1-Hexene	W. Germany 2,421,556	1975	Gulf Research
Molding resins	Ethylene	Japan 135,349	1977	Kansai Paint
Thermoplastic moldings, laminates	Ethylene	United States 4,073,827	1978	Toray Industries, Inc.
Moldings, coatings and adhesives	Ethylene	Japan 1,519	1978	Toyo Soda
Compositions for mold castings	Isobutylene	Japan 127,323(4)	1978	Hitachi, Ltd.
Epoxy molding compositions	$\alpha$ -Olefins	United States 4,167,539	1979	Gulf Oil
Electrochemical cell diaphragm	Ethylene	Europe 1,664	1979	Solvay & Cie
Molding compositions	$\alpha$ -Olefins	Japan 110,148	1980	Oshika Shinko
Heat sensitive recording material	Isobutylene	Japan 164,193	1980	Sanyo
<i>POLYMER ADDITIVES</i>				
Natural rubber stabilizer	Ethylene	United States 3,284,220	1966	Monsanto
Plasticizer extender	Ethylene	United States 3,437,692	1969	Eastman Kodak
Asphalt modifier	$C_{15}$ - $C_{20}$ $\alpha$ -olefins	United States 3,531,426	1970	Mobil Oil
PVC stabilizer	Ethylene	United States 3,629,205	1971	Stauffer Chemical
Polyamide modifier	Ethylene, 1-hexene	United States 3,644,571	1972	Gulf Research
Polyolefin dye acceptor additive	Ethylene	France 2,123,904	1972	Ethylene-Plastique
Vinyl polymer stabilizer	Ethylene	United States 3,725,508	1973	Stauffer Chemical
Polyamide modifier moldings, laminates	Ethylene	United States 3,781,381	1973	Union Carbide
Polyolefin thermoplastic additives	Ethylene	United States 3,856,724	1974	Texaco
PVC modifiers and plasticizer	Dicyclopentadiene	Japan 4,552	1974	Arakawa Forest Chemical Ind.
Paper and polyolefin reinforcer additive	Ethylene	Japan 118,916	1974	Sumitomo Chemical
Polyolefin modifier—synthetic paper	Ethylene	Britain 1,401,599	1975	Gulf Research
Polyolefin adhesion promoter	Propylene	Japan 50,456	1975	Mitsui Petrochemical
Isoprene rubber modifier	Isobutene, isoprene	Japan 126,746	1975	Kuraray

PVC stabilizer	Ethylene	United States 4,036,810	1977	Hooker Chemical
Paper coatings, rubber additives	Diisobutylene, isobutylene, ethylene	United States 4,048,442	1977	Bayer, Akt.
PVC stabilizer, plasticizer	Ethylene	United States 4,055,581	1977	Hooker Chemical
Modifier for polyethylene terephthalate production	Ethylene	Netherlands 3,890	1977	Chemische Werke Huels
Reversible resins coatings, dyeing aids, tackifying agent	Butadiene	Netherlands 4,408	1977	Nippon Oil
Reversible resins coatings, dyeing aids, tackifying resins	Butadiene, isoprene, piperylene	United States 4,072,646	1978	Nippon Oil
Plasticizers for PVC	Ethylene	United States 4,077,935	1978	W. R. Grace
Plastics lubricants	C <sub>8</sub> -C <sub>24</sub> $\alpha$ -olefins	Belgium 871,549	1979	AKZO G.m.b.H.
Plastics processing aids	C <sub>8</sub> -C <sub>22</sub> $\alpha$ -olefins	W. Germany 2,748,367	1979	AKZO G.m.b.H.
Lustre-imparting additives	C <sub>28</sub> -C <sub>60</sub> $\alpha$ -olefins	Japan 75,487	1979	Mitsubishi Chemical
Water-quenching additives	Butadiene	Japan 102,212	1979	Nippon Oil
Zn salt stabilizer for flame-resistant thermoplastics	Diisobutylene	W. Germany 2,827,760	1980	BASF A.G.
Drying aid for aqueous dispersions of thermoplastics	Ethylene	Japan 56,133	1980	Mitsui Petrochemical

PAPER MODIFIER

Wax extender for paper	1-Octadecene	United States 2,599,339	1952	Standard Oil
Textile sizing agent, paper sizing resins	Diisobutylene	United States 2,725,367	1955	Rohm & Haas
Paper retention agents	Diisobutylene	United States 2,838,397	1958	Rohm & Haas
Paper sizing resins	Ethylene	United States 3,000,840	1961	Monsanto
Paper sizing adhesives, waxes, polishes, coatings	Isobutylene	United States 3,053,814	1962	Monsanto
Paper laminates	Ethylene	W. Germany 1,147,382	1963	Henkel & Cie
Paper sizing resins	1-Octadecene	Netherlands 12,318	1965	Monsanto
Sizing for paper	1-Octadecene	United States 3,291,679	1966	Monsanto
Paper coatings	1-Octadecene	Belgium 668,199	1966	Monsanto
Paper sizing agent	1-Octadecene	United States 3,382,142	1968	Monsanto
Paper sizing resins	Ethylene	France 1,534,563	1968	Henkel & Cie

Table A.3 (cont.)

Applications	Olefins	Patent	Year	Assignee
Sizing for cellulose, pottings com-positions	1-Hexene, 1-decene, 1-octadecene	United States 3,459,715	1969	Monsanto
Carbonless coated capsules	Ethylene	France 1,565,952	1969	National Cash Register
Paper sizing polyolefin coatings	Diisobutylene	United States 3,494,783	1970	Phillips Petroleum
CaCO <sub>3</sub> dispersant binder for paper coatings	Ethylene	United States 3,597,251	1971	Wyandotte Chemical
Paper sizing resins	Cracked gasoline	Britain 1,291,812	1972	M. Takahara
Electrostatic paper coatings	Ethylene	W. Germany 2,237,008	1973	Ricoh
Paper sizing agents	Ethylene	Japan 6,406	1973	Arakawa Forest Chemical Ind.
Paper sizing agents	Isobutene	Japan 6,407	1973	Kuraray
Paper sizing agents	Propylene	Japan 6,408	1973	Kuraray
Rosin substitute paper sizing resins	Cyclopentadiene, dicyclopentadiene	Japan 6,942	1973	Arakawa Forest Chemical Ind.
Paper sizing resins	Ethylene	Japan 23,801	1973	Toho Chemical Ind.
Paper coatings	Isobutene	Japan 41,447	1973	Kuraray
Paper coatings	Propylene	Japan 41,764	1973	Kuraray
Electroconductive paper coatings	Isobutene	Japan 51,289	1973	Kuraray
Paper sizing agent	Octadec-9-ene	United States 3,821,069	1974	National Starch
Paper sizing resins	1-Hexene	United States 3,853,609	1974	Nalco Chemical
Electrical conductive paper coatings	Isobutene	Japan 11,453	1974	Kuraray
Paper and textile coatings	Isobutene	Japan 11,853	1974	Kuraray
Paper coatings	Ethylene butenes	Japan 24,802	1974	Kuraray
Paper coatings	Isobutene, butadiene	Japan 29,124	1974	Kuraray
Paper coatings	Isobutene	Japan 30,611	1974	Kuraray
Paper sizing agent	1-Hexene	United States 3,868,353	1975	E. E. Allen
Paper sizing agent	Diisobutylene	W. Germany 2,361,544	1975	Bayer A.G.
Paper coatings	Ethylene	W. Germany 2,429,029	1975	Kanzaki Paper Mfg.
Paper sizing resins	Ethylene	Japan 5,285	1975	Arakawa Forest Chemicals



Paper coatings	Isobutylene	Japan 53,607	1975	Kuraray
ZnO binder—electric recording paper	Isobutylene	Japan 73,046	1975	Tomoe-gawa Paper Mfg.
Metal oxide carrier, recording paper	Isobutylene	Japan 73,047	1975	Tomoe-gawa Paper Mfg.
Paper sizing coatings	C <sub>2</sub> –C <sub>8</sub> $\alpha$ -olefins	W. Germany 2,501,123	1976	Bayer A.G.
Thickener, paper sizing	Methyl cyclopentadiene	United States 4,012,575	1977	Borg–Warner
Paper coatings, rubber additives	Diisobutylene, isobutylene, ethylene	United States 4,048,422	1977	Bayer, Akt.
Paper sizing agents	C <sub>10</sub> –C <sub>26</sub> $\alpha$ -olefins	United States 4,065,608	1977	Akazona, Inc.
Thickener, stabilizer, textile and paper coatings	Butadiene	W. Germany 1,795,660	1977	Borg–Warner
Adhesives, coatings, dispersant, textile and paper sizing	Dicyclopentadiene	W. Germany 2,656,830	1977	Borg–Warner
Paper sizing agents	C <sub>4</sub> and C <sub>5</sub> cuts	Europe 1,868	1979	VEBA Chemical
Paper coatings	Diisobutylene	Japan 18,911	1979	Kuraray
Heat-sensitive paper coatings	Isobutylene	Japan 85,039(40)	1979	Hitachi Maxell
Paper coatings	Diisobutene	Japan 101,908	1979	Kuraray
Anionic paper sizing resins	Cyclopentadiene	United States 4,200,559	1980	Seiko Seiki
Paper sizing	Dicyclopentadiene	Europe 15,028	1980	Chemische Werke Huels
Paper surface sizing compositions	C <sub>8-12</sub> $\alpha$ -olefins	W. Germany 2,835,224	1980	BASF A.G.
Foam-poor surface sizing for paper	Diisobutylene	W. Germany 2,840,650	1980	Bayer A.G.
Paper sizes	Dicyclopentadiene	W. Germany 2,905,764	1980	Chemische Werke Huels
Electrorecording paper coatings	Isobutylene	Japan 12,873	1980	Tomoe-gawa Paper Mfg.
Antistatic coatings—photographic paper	C <sub>3-8</sub> $\alpha$ -olefins	Japan 14,415	1980	Konishiroku Photo
Paper sizing resins	C <sub>30-60</sub> $\alpha$ -olefins	Japan 16,928	1980	Mitsubishi Chemical
Paper sizing compositions	Diisobutylene	Japan 67,094(95)	1980	—
Pitch prevention agents for paper-making process	Isobutylene, diisobutylene	Japan 84,491	1980	Nippon Oils and Fats
Anionic paper sizing agents	Diisobutylene	U.S.S.R. 704,466	1980	Bayer A.G.
Imide salts as paper sizing	2,4,4-Trimethylpenter-1	Europe 706	1981	Bayer A.G.

Table A.3 (cont.)

Applications	Olefins	Patent	Year	Assignee
<i>POLYMER ALLOYS</i>				
Foamable polymeric alloy compositions	Ethylene	United States 4,207,402	1980	Monsanto
Injection moldings	Ethylene	Japan 9,522	1981	Ethylene Plastique S.A.
<i>PRINTING INKS</i>				
Electrophotographic printing resins	Ethylene	Netherlands 300,364	1965	Charles Bruning
Printing ink	Methyl dicyclopentadiene	W. Germany 2,352,621	1972	Toyo Ink Mfg.
Printing ink resins	Ethylene	W. Germany 2,414,558	1974	Nippon Oil
Pressure-sensitive ink coatings—Microencapsulation	Ethylene	W. Germany 2,529,427	1976	National Cash Register
Printing ink resins	Cyclopentadiene	Belgium 861,508	1978	BASF A.G.
Printing ink compositions	Cyclopentadiene, methylcyclopentadiene	Japan 37,845	1979	Arakawa Rinsan Kaga
Microencapsulation coatings	Isobutylene	Japan 85,184	1979	Fuji Photo Film
Carbon paper inks	C <sub>20-50</sub> $\alpha$ -olefins	Japan 58,272	1980	Nippon Oil
Pressure-sensitive copying paper	Isobutylene	Japan 75,736	1980	Kuraray
<i>PROTEIN FIXING AGENTS</i>				
Protein carrier	Ethylene	W. Germany 1,935,711	1970	Boehringer Mannheim G.m.b.H.
Polypeptide separator	Ethylene	South Africa 4,725	1970	Farbenfabriken Bayer A.G.
<i>SEALANTS/CAULKS</i>				
Sealants for membranes	Ethylene	France 1,534,286	1968	National Cash Register
Liquid crystal cell sealants	Butadiene	W. Germany 2,365,226	1974	Dai Nippon Tonyo

Container gaskets	Ethylene	United States 4,020,966	1977	W. R. Grace
Container gaskets	Ethylene, propylene	United States 4,128,185	1978	W. R. Grace
Caulking compositions	Isobutylene	Japan 110,262	1979	Kasei
WATER-SOLUBLE POLYMERS				
Polyelectrolytes, amides	Isobutylene	W. Germany 925,735	1955	Monsanto
Amide salts—drilling fluid additives	Isobutylene	United States 2,826,548	1958	Monsanto
Flocculating agents, oil well drilling additive	Isobutylene	United States 2,847,403	1958	Monsanto
Alkali-soluble resins	Ethylene, propylene, butenes	United States 2,857,365	1958	Monsanto
Amide salts for drilling mud additive	Ethylene	United States 2,911,366	1959	Monsanto
Oil well drilling additives	Ethylene	United States 2,913,437	1959	Monsanto
Polyampholytes	Ethylene	United States 2,914,510	1959	Monsanto
Drilling mud additives, inorganic pigment dispersants	Ethylene, propylene, isobutylene	United States 2,938,016	1960	Monsanto
Drilling mud additive	Ethylene	United States 2,948,678	1960	Magnet Cove Barium Corp.
Oil well drilling additives	Ethylene	Britain 851,237	1960	Monsanto
Drilling mud additives	Ethylene	United States 2,979,454	1961	Monsanto
Oil well drilling mud additive	Ethylene	United States 3,070,544	1962	Monsanto
Gelatin hardener, photographic films	Ethylene	W. Germany 1,149,517	1963	Henkel & Cie
Flocculants—water purification	Isobutylene	United States 3,157,595	1964	Monsanto
Extrudable alcohol gels	Ethylene	France 1,348,302	1964	Colgate-Palmolive
Polyelectrolytes	Isobutylene	Netherlands 5,547	1964	Imperial Chemical
Thickening agent, textile printing inks	Ethylene	United States 3,165,486	1965	Monsanto
Clay beneficiation agent	Ethylene, propylene, butenes	United States 3,216,934	1965	Monsanto
Viscosity builder—bentonite clay	Ethylene	United States 3,220,946	1965	Magnet Cove Barium Corp.
Drilling mud additives	Ethylene	United States 3,222,278	1965	Monsanto
Polyelectrolyte coagulants (flocculants)	Ethylene, propylene, butenes	France 1,391,814	1965	Monsanto
Thickeners	Ethylene	Netherlands 4,619	1966	Imperial Chemical



Table A.3 (cont.)

Applications	Olefins	Patent	Year	Assignee
Gelatin hardener—photographic films	Ethylene	United States 3,330,664	1967	Eastman Kodak
Polyelectrolytes	Ethylene	United States 3,340,680	1967	Monsanto
Polyampholytes—water purification	Ethylene	United States 3,398,092	1968	Monsanto
Thickeners	Dicyclopentadiene, propylene	France 1,510,303	1968	Farbwerke Hoechst
Aqueous dye solution thickeners	Ethylene	W. Germany 1,904,309	1970	Diamalt A.G.
Waste water purification resins	Isobutylene	W. Germany 1,945,749	1970	Monsanto
Microbiological nutrient media modifier	Ethylene	W. Germany 2,011,366	1970	Union Carbide
Thickeners	Ethylene	Britain 1,241,294	1971	Imperial Chemical
Kaolin clay flocculant	Isobutylene	W. Germany 1,570,915	1971	Monsanto
Thickening agent, cosmetics dispersant	Ethylene	W. Germany 2,113,213	1971	GAF
Thixotropic additive	Propylene	Czechoslovakia 146,293	1972	K. Hajek
Drilling mud additive	Ethylene	France 2,183,838	1974	Monsanto
Flocculant—water clarification	Diisobutylene	United States 3,929,635	1975	Petrolite
Thickening agent—photographic gelatin solutions	Isobutylene, diisobutylene	Japan 67,318	1975	Fuji Photo Film
Water-soluble adhesives, thickeners, binders, coatings	Butadiene, isoprene	W. Germany 2,547,556	1976	Nippon Oil
Flocculant water clarifier	Isobutylene	Japan 32,053	1976	Kuraray
Flocculant—photographic film	Ethylene	W. Germany 2,641,703	1977	Fuji Photo Film
Water-soluble quenching agents for metals	Butadiene, isoprene	United States 4,090,891	1978	Nippon Oil
Reversible resins, aqueous adhesives, thickeners, binders, coatings	Butadiene, isoprene	Britain 1,525,004	1978	Nippon Oil
Reversible resins	Butadiene	Japan 20,553	1978	Nippon Oil
Release coatings	1-Octadecene	United States 4,118,541	1979	Formica Corp.
Photographic coatings and thickness	Isobutylene	United States 4,166,050	1979	Fuji Photo Film
Thickeners and thinning agents	Indene	Netherlands 1,707	1979	Standard Oil
Solid-liquid phase reversible systems	Butadiene, isoprene	Britain 1,588,154	1981	Nippon Oil

Table A.4. Alkyl Vinyl Ether–Maleic Anhydride Copolymer Patents

Applications	Ethers	Patent	Year	Assignee
<i>PRODUCTION PROCEDURE</i>				
Production procedure	Methyl vinyl	United States 2,047,398	1936	GAF
Production procedure	Methyl vinyl	United States 2,300,566	1942	GAF
Amide production procedure	Methyl vinyl	United States 2,313,565	1943	Eastman Kodak
Production procedure, propyl, etc. vinyl	Methyl, ethyl	United States 3,706,703	1972	Gulf Research
Production procedures	Isobutyl vinyl	E. Germany 128,163	1977	VEB Leung-Werke
Production procedure for powders	Methyl, ethyl, etc. vinyl	W. Germany 2,014,242	1979	GAF
Calcium salt derivatives	Divinyl	United States 4,223,109	1980	Adria Laboratories Inc.
Improved production procedure	Methyl, ethyl, etc. vinyl	Japan 145,714	1980	Daikin Kogyo

ADHESIVES

Water-moistenable adhesives	Methyl vinyl	United States 2,667,462	1954	Monsanto
Coatings and adhesives	Methyl, isobutyl, etc. Vinyl	United States 2,694,697(8)	1954	GAF
Adhesives and coatings	Methyl, ethyl, propyl, etc. vinyl	Britain 712,220	1954	GAF
Coatings, adhesives	Methyl vinyl	United States 2,744,098	1956	GAF
Adhesives	Methyl vinyl	United States 2,782,182	1957	GAF
Aluminum foil adhesives	Methyl vinyl	United States 2,785,993	1957	Celanese
Water-moistenable adhesives	Methyl vinyl	United States 2,793,966	1957	Nashua
Water-moistenable adhesives	Methyl vinyl	United States 2,808,381	1957	Pailsey Products
Splicing-tape adhesives	Methyl vinyl	United States 2,838,421	1958	3M
Pressure-sensitive adhesives	Methyl vinyl	United States 2,855,722(5)	1958	Johnson & Johnson
Adhesives	Methyl vinyl	United States 2,864,803	1958	B.F. Goodrich
Surgical adhesives, resins	Methyl vinyl	Britain 798,806	1958	Johnson & Johnson
Liquid mucilages, adhesives	Methyl vinyl	Britain 803,231	1958	B.F. Goodrich
Plastics adhesive	Methyl vinyl	United States 2,895,866	1959	GAF
Paper, glass, metal, wood adhesives	Methyl vinyl	W. Germany 1,054,930	1959	GAF

Table A.4 (cont.)

Applications	Ethers	Patent	Year	Assignee
Adhesives	Methyl vinyl	United States 2,922,775	1960	General Electric
Thermoset resins	Methyl vinyl	United States 2,935,484	1960	B.F. Goodrich
Rewettable adhesives	Methyl vinyl	Britain 830,938	1960	GAF
Orthopedic bandage adhesives	Methyl vinyl	Britain 834,063	1960	T.J. Smith Nephew Ltd.
Food package adhesives	Methyl vinyl	United States 2,978,343	1961	National Starch
Surgical dressings	Methyl vinyl	United States 2,997,464	1961	Johnson & Johnson
Pressure-sensitive adhesives	Methyl vinyl	United States 3,002,954(5)	1961	Johnson & Johnson
Aqueous pressure-sensitive adhesives	Methyl vinyl	Britain 941,276	1963	Norton
Paper laminate adhesives	Methyl vinyl	United States 3,133,890	1964	Borden
Adhesives, coatings	Methyl, ethyl, etc. vinyl	France 1,400,133	1965	Badische Anilin
Moldings, films, lubricant additives, adhesives	Divinyl	United States 3,320,216	1967	Peninsular Chemresearch
Adhesives	Methyl, ethyl, etc. vinyl	France 1,506,778	1967	GAF
Dextrin adhesives modifier	Methyl vinyl	United States 3,366,587	1968	GAF
Adhesives	Ethyl vinyl	United States 3,395,033	1968	Inca Inks
Wallpaper paste resins	Methyl, ethyl, etc. vinyl	Britain 1,117,515	1968	Imperial Chemical
Adhesives	Methyl vinyl	Japan 25,982	1968	Mitsubishi Petrochemical
Paper and textile adhesives	Methyl vinyl	United States 3,462,342	1969	Battelle Development Corp.
Adhesive, coatings	Methyl vinyl	United States 3,532,771	1970	GAF
Water-resistant adhesives	Methyl vinyl	Japan 10,799	1971	K. Yazawa
Aluminum—paper adhesives	Methyl vinyl	Japan 17,440	1971	Hekisto Gosei
Adhesives, remoistenable labels	Methyl vinyl	Canada 911,629	1972	Charles Tennant
Aqueous pressure-sensitive adhesives	Methyl vinyl	W. Germany 2,143,586	1972	Imperial Chemical
Plywood adhesives	Methyl vinyl	Japan 27,242	1972	Kuraray
Carton sealing adhesives	Methyl vinyl	United States 3,730,925	1973	Anheuser-Busch
Water-soluble pressure-sensitive adhesives	Methyl vinyl	Britain 1,327,847	1973	3M



Aqueous pressure-sensitive adhesives	Methyl vinyl	W. Germany 2,311,746	1973	Beiersdorf A.G.
Release coatings—pressure-sensitive adhesives	Methyl, ethyl etc. vinyl	United States 3,803,068	1974	GAF
Tobacco substitute binder	Methyl vinyl	United States 3,842,845	1974	Celanese
Heat sealable, remoistenable adhesives	Octadecyl vinyl	Britain 1,383,406	1975	GAF
Stationary adhesives	Methyl vinyl	Japan 46,745	1975	Konishi Gisuke
Adhesives	Methyl vinyl	Japan 117,832	1975	Konishi Gisuke
Pressure-sensitive adhesives	Methyl vinyl	Canada 984,084	1976	Consolidated–Bathurst

BOILER SCALE CONTROL AGENT

Boiler scale remover	Methyl vinyl	.United States 2,723,956	1955	National Aluminate
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CELLULAR MATERIALS

Cellular plastics	tert-butyl vinyl	United States 3,298,972	1967	Monsanto
Cellular plastics	tert-butyl vinyl	United States 3,299,012	1967	Monsanto
Foams, coatings	Methyl vinyl	W. Germany 1,939,696	1970	Koppers

COATINGS

Coatings	Methyl vinyl	United States 2,156,069	1939	GAF
Coatings	Methyl vinyl	United States 2,215,196	1940	GAF
Coatings	Methyl vinyl	United States 2,261,295	1941	GAF
Glass lamp coatings	Methyl vinyl	United States 2,287,414	1941	General Electric
Coatings	Methyl vinyl	Holland 61,145	1948	N.V. de Bataafsche Petroleum
Moldings and coatings	Methyl, ethyl, etc. vinyl	United States 2,543,601(602)	1951	Rohm & Haas
Glass fiber coatings	Methallyl alkyl	United States 2,611,718	1952	Owens Corning
Coatings and adhesives	Methyl, isobutyl etc. vinyl	United States 2,694,697(8)	1954	GAF
Adhesives and coatings	Methyl, ethyl, propyl, etc. vinyl	Britain 712,220	1954	GAF
X-Ray print modifiers	Methyl vinyl	United States 2,649,372	1955	GAF

Table A.4 (cont.)

Applications	Ethers	Patent	Year	Assignee
Photomechanical resins	Methyl vinyl	United States 2,719,141	1955	Eastman Kodak
Hair spray resins	Methyl vinyl	United States 2,723,248	1955	GAF
Thermoset resins	Methyl vinyl	Japan 6,492	1955	3M
Photographic antihalation layers	Methyl vinyl	United States 2,732,305	1956	GAF
Coatings, adhesives	Methyl vinyl	United States 2,744,098	1956	GAF
Photographic film additive	Methyl vinyl	United States 2,772,165	1956	DuPont
Photoactive resins	Methyl vinyl	United States 2,816,091	1957	Eastman Kodak
Phosphorus binder coatings	Methyl vinyl	W. Germany 1,012,175	1957	General Electric
Fluorescent tube coatings	Methyl vinyl	United States 2,832,309	1958	General Electric
Silver halide-gelatin stabilizer— Photographic films	Methyl vinyl	United States 2,836,769	1958	DuPont
Coatings	Methyl vinyl	United States 2,848,350	1958	Tru-Scale
Photographic films	Methyl vinyl	United States 2,854,338	1958	GAF
Photographic antihalation layer	Butyl vinyl	Britain 790,023	1958	Agfa A.G.
Incandescent lamp coatings	Methyl vinyl	W. Germany 1,028,230	1958	General Electric
Thermoset resins	Methyl vinyl	United States 2,882,257	1959	GAF
Ultraviolet filters	Methyl vinyl	United States 2,901,390	1959	GAF
Light-sensitive coatings	Methyl vinyl	W. Germany 1,056,931	1959	Harris Intertype
Water-based paints	Methyl vinyl	Britain 845,019	1960	B.F. Goodrich
Fluorescent tube coatings	Methyl vinyl	Japan 4,768	1960	Hitachi Lamp
Press plate coatings	Methyl vinyl	United States 2,983,220	1961	Timefax
Fluorescent tube coatings	Methyl vinyl	United States 2,987,414	1961	General Electric
Fluorescent lamp coatings	Methyl vinyl	United States 3,006,781	1961	General Electric
Adhesives, sizings, hair spray resins	Methyl vinyl	Britain 863,379	1961	GAF
Press plate coatings	Methyl vinyl	Britain 864,033	1961	Harris Intertype
Pressure-sensitive release coatings	Octadecyl vinyl	Britain 864,483	1961	Adhesives Tapes Ltd.
Press plate coatings	Methyl vinyl	Britain 880,051	1961	GAF
Press plate coatings	Methyl vinyl	Britain 889,363	1962	GAF
Metal surface coatings	Methyl vinyl	Britain 893,019	1962	Pyrene

Photographic subbing layer	Methyl vinyl	United States 3,072,482	1963	Keuffel & Esser
Press plate coatings	Methyl vinyl	United States 3,086,861	1963	GAF
Photographic film coatings	Methyl vinyl	Belgium 630,170	1963	Agfa A.G.
Photographic film coatings	Methyl vinyl	Belgium 669,393	1963	Fuji Photo Film
Hair spray resins	Methyl vinyl	Britain 944,439	1963	Gillette
Noncurling photographic print coatings	Methyl vinyl	W. Germany 1,156,651	1963	Agfa A.G.
Metal coatings	Methyl vinyl	United States 3,132,055	1964	Yawata Iron & Steel
Metal coatings	Methyl vinyl	Belgium 637,222	1964	Societe Continentale Parker
Coatings for metallic films	Methyl vinyl	Britain 954,566	1964	Farbwerke Hoechst A.G.
Paper coatings	Isobutyl vinyl	W. Germany 1,696,162	1964	BASF A.G.
Hair spray resins	Methyl vinyl	Netherlands 5,355	1964	Oreal, S.A.
Pressure- and Heat-sensitive recording resins	Methyl vinyl	Belgium 663,660	1965	National Cash Register
Adhesives coatings	Methyl, ethyl, etc. vinyl	France 1,400,133	1965	Badische Anilin
Antistatic film coatings	Methyl vinyl	France 1,414,003	1965	Kodak-Pathe
Thermosetting resins	Methyl, ethyl, etc. vinyl	W. Germany 1,207,532	1965	Henkel & Cie
Diazo coatings for vesicular sub-strates	Methyl vinyl	United States 3,244,523	1966	Allied Paper
Transparent, reflective coatings	Methyl vinyl	United States 3,290,203	1966	3M
Lithographic printing plate coatings	Methyl vinyl	W. Germany 1,213,437	1966	GAF
Thickeners, coatings	Methyl vinyl	Netherlands 4,619	1966	Imperial Chemical
Xerographic pigments	Methyl vinyl	Netherlands 8,583	1966	Rank-Xerox
Antistatic coatings—plastics film	Methyl vinyl	Britain 1,066,188	1967	Bexford Ltd.
Water-based enamels	Methyl, ethyl, etc. vinyl	France 1,465,525	1967	DuPont
Zinc phosphate coatings on steel	Methyl, ethyl, cyclohexyl, etc. vinyl	W. Germany 2,248,867	1967	Dulux Australia
Thermosetting aqueous resins	Methyl vinyl	Netherlands 10,969	1967	National Starch
Electrophotographic printing plate resins	Methyl vinyl	Netherlands 13,230	1967	GAF
Water-repellent coatings	Tridecyl vinyl	United States 3,410,720	1968	Monsanto
Dye carrier—hair spray resins	Methyl vinyl	France 1,517,862	1968	Oreal S.A.



Table A.4 (cont.)

Applications	Ethers	Patent	Year	Assignee
Hair spray lacquers	Methyl vinyl	France 1,530,342	1968	Precision Valve
Nail polish resin	Methyl vinyl	France 1,547,495	1968	Oreal S.A.
Skin and hair coatings	Methyl vinyl	South Africa 6,049	1968	Gillette
Phosphorus lamp coating binder	Methyl vinyl	United States 3,420,625	1969	General Electric
Chemical-nickel plating coatings— active metal coatings	Methyl vinyl	United States 3,424,597	1969	Shipley
Waterborne coatings	Methyl vinyl	United States 3,425,977	1969	National Starch
Waterproof match striker coatings	Methyl, ethyl, etc. vinyl	United States 3,411,456	1969	GAF
Photoactive resins	Methyl vinyl	United States 3,448,089	1969	DuPont
Strippable metal coatings	Methyl vinyl	Britain 1,170,823	1969	Imperial Chemical
Photosensitive polymers—image formation coatings	Methyl, ethyl, isobutyl, dodecyl, etc. vinyl	France 1,555,957	1969	GAF
Color television tube coatings	Methyl vinyl	France 1,572,309	1969	GAF
Antistatic coatings—photographic films	Methyl vinyl	W. Germany 1,923,417	1969	GAF
Nacreous pigment binder	Methyl vinyl	South Africa 5,748	1969	Nay & Baker Ltd.
Thermosetting resins	Methyl vinyl	United States 3,429,999	1970	Pacific Vegetable Oil
Wash primer coatings	Methyl vinyl	United States 3,528,860	1970	Oakite Products
Floor polish compositions	Methyl vinyl	United States 3,532,656	1970	Gulf Research
Adhesive coatings	Methyl vinyl	United States 3,532,771	1970	GAF
Photographic fixation layer coatings	Methyl vinyl	France 1,591,741	1970	Kodak Pathe
Photoactive resins	Methyl vinyl	France 2,009,112	1970	GAF
Polyester photographic film subbing layer resin	Methyl, ethyl, butyl, etc. vinyl	France 2,221,750	1970	Fuji Photo Film
Foams, coatings	Methyl vinyl	W. Germany 1,939,696	1970	Koppers
Hair setting resins	Methyl vinyl	W. Germany 1,946,405	1970	3M
Metal finishes antitarnish coatings	Methyl vinyl	W. Germany 2,014,883	1970	Miles Laboratories
Fertilizer coatings, slow-release coatings	Methyl vinyl	W. Germany 2,019,724	1970	3M

Photoactive resins, photographic films	Methyl vinyl	W. Germany 2,122,036	1970	GAF
Photoactive resins	Methyl vinyl	W. Germany 2,123,623	1970	Upjohn
Fluorescent lamp coatings	methyl vinyl	Japan 7,421	1970	Tokyo Shibaura Electric
UV hardenable resin	Methyl vinyl	United States 3,562,269	1971	Upjohn
Water-repellent finish	Octadecyl vinyl	United States 3,578,488	1971	A.G. Ohlhausen
Photoresist resins	Methyl vinyl	United States 3,594,243	1971	GAF
Abrasion resistant glass coatings	Methyl vinyl	United States 3,598,632	1971	Owens-Illinois
Hair spray resins	Methyl vinyl	United States 3,630,654	1971	Bristol-Meyers
Detergent granule coatings	Methyl vinyl	United States 3,630,920	1971	GAF
Abrasion-resistant glass coatings	Methyl vinyl	France 2,057,339	1971	Owens-Illinois
Abrasion-resistant glass coatings	Methyl vinyl	W. Germany 1,940,728	1971	Owens-Illinois
Photoresist coatings supports	Methyl vinyl	W. Germany 2,046,115	1971	Shipley
Hair spray resins	Methyl vinyl	W. Germany 2,063,909	1971	Ciba-Geigy
Lithographic printing plate coatings	Methyl vinyl	W. Germany 2,100,217	1971	Eastman Kodak
Photoactive dye coatings	Methyl vinyl	W. Germany 2,107,394	1971	Upjohn
Photoactive resins, photoresists	Methyl vinyl	W. Germany 2,108,734	1971	Upjohn
Polyolefin bonded coating	Methyl vinyl	South Africa 4,244	1971	Upjohn
Liquid tonor modifier	Methyl, ethyl, octadecyl, etc. vinyl	South Africa 7,564	1971	GAF
Antifriction coating lacquers	Butyl vinyl	U.S.S.R. 301,078	1971	State Scientific Research Institute for Plastics
Photoresist resins	Methyl, ethyl, etc. vinyl	United States 3,649,283	1972	Shipley
Radiation-sensitive resins	Methyl vinyl	United States 3,652,599	1972	Upjohn
Photoresist resins	Methyl vinyl	United States 3,657,199	1972	Upjohn
Rubber coatings	Methyl vinyl	United States 3,669,718	1972	Dow Chemical
Antistatic coatings—photographic films	Methyl vinyl	United States 3,676,209	1972	GAF
Printing and photoresist coatings	Methyl vinyl	United States 3,699,080	1972	Upjohn
Electron-sensitive (radiation-curable) resins	Methyl vinyl	United States 3,703,402	1972	General Electric
Photoactive resins—photoresists	Methyl vinyl	Britain 1,259,918	1972	Upjohn
Abrasion-resistant glass coatings	Methyl vinyl	Britain 1,267,855	1972	Owens-Illinois
Photoactive resins, photoresists	Methyl vinyl	W. Germany 2,033,687	1972	Upjohn

Table A.4 (cont.)

Applications	Ethers	Patent	Year	Assignee
Antistatic coatings—photographic films	Butyl vinyl	W. Germany 2,144,286	1972	Fuji Photo Film
Hair spray resins	Methyl vinyl	W. Germany 2,150,619	1972	Gillette
Hydrophilic binders—offset printing plates	Methyl vinyl	W. Germany 2,165,358	1972	Mitsubishi Paper Mills
Electrophotographic coatings	Methyl, ethyl, etc. vinyl	W. Germany 2,210,140	1972	Canon KK
Nitromethane explosives coatings	Methyl vinyl	United States 3,713,915	1973	Amoco Production
Photographic diffusion—transfer film binder	Methyl vinyl	United States 3,756,815	1973	Polaroid
Radiation-sensitive resins	Methyl vinyl	United States 3,763,118	1973	Upjohn
Radiation-sensitive resins	Methyl vinyl	United States 3,770,846	1973	Upjohn
Hair setting agent	Methyl vinyl	Britain 1,321,836	1973	Imperial Chemical
Concrete coatings	Methyl vinyl	W. Germany 2,152,876	1973	Lord
Mold release agents	Octadecyl vinyl	W. Germany 2,250,731	1973	GAF
Photosensitive printing plate resins	Methyl vinyl	W. Germany 2,251,030	1973	Fuji Photo Film
Color diffusion coating—photographic films	Isobutyl vinyl	W. Germany 2,300,174	1973	Polaroid
Electrophotographic coatings	Methyl vinyl	W. Germany 2,303,819	1973	Addressograph—Multigraph
Coatings	Furfuryl vinyl	U.S.S.R. 371,200	1973	Irkutsk Institute of Organic Chemistry
Photoresist resins	Methyl vinyl	United States 3,792,025	1974	Upjohn
Photoactive resins	Octadecyl vinyl	United States 3,794,626	1974	Upjohn
Release coatings—pressure-sensitive adhesives	Methyl, ethyl, etc. vinyl	United States 3,803,068	1974	GAF
Photosensitive copying resins	Methyl vinyl	United States 3,808,006	1974	3M
Reversible shear thinning gel—glass fiber coatings	Methyl, ethyl, etc. vinyl	United States 3,810,784	1974	Owens—Corning Fiberglass
Amine scavenger—thermosetting resins	Methyl vinyl	United States 3,820,290	1974	Norton
Photographic films coatings	Methyl vinyl	United States 3,820,990	1974	Eastman Kodak



Hydrophilic polyurethane foam coatings	Methyl vinyl	United States 3,826,674	1974	Kimberly-Clark
Nail polish dye binder	Methyl vinyl	United States 3,849,547	1974	Oreal S.A.
Photosensitive lithographic plate coatings	Methyl vinyl	United States 3,856,523	1974	Upjohn
Radiation-sensitive resins	Methyl vinyl	France 2,182,999	1974	Upjohn
Photoresist coatings	Methyl vinyl	France 2,227,558	1974	W.R. Grace
Electrophotographic film barrier layer	Methyl vinyl	France 2,231,991	1974	Eastman Kodak
Paperboard coatings	Isobutyl vinyl	W. Germany 1,696,162	1974	BASF A.G.
Light-sensitive resins	Methyl vinyl	W. Germany 2,319,848	1974	W.R. Grace
Electrophotographic liquid tonor additives	Octadecyl vinyl	W. Germany 2,354,259	1974	GAF
Electrophotographic recording coatings	Methyl, ethyl, etc. vinyl	W. Germany 2,355,389	1974	Canon KK
Fluorescent lamp coatings	Methyl vinyl	Japan 18,097	1974	Hitachi, Ltd.
Rubber roller coatings	Methyl vinyl	Japan 20,751	1974	Yamauchi Rubber
Printing plate coatings	Methyl vinyl	Japan 37,701	1974	Nippon Oil Seal
Photographic film antiretication coatings	Methyl vinyl	Japan 106,821	1974	Fuji Photo Film
Photocrosslinkable coatings—photo-graphic films	Methyl vinyl	Japan 128,992	1974	Agency of Industrial Science & Technology
Photocrosslinkable resins—photo-graphic films	Isobutyl vinyl	Japan 128,993	1974	Agency of Industrial Science & Technology
Photoresist resins	Methyl vinyl	Netherlands 5,548	1974	W.R. Grace
Photoconductive recording sheet interlayer	Methyl vinyl	United States 3,860,422	1975	Canon KK
Hair spray resins	Steryl vinyl	United States 3,862,306	1975	Gillette
Antihalation layer—photographic films	Methyl vinyl	United States 3,869,402	1975	GAF
Radiation active polyolefin coatings	Methyl vinyl	United States 3,911,164	1975	Upjohn
Zn phosphate metal coatings modifier	Methyl, ethyl, cyclohexyl, etc. vinyl	Australia 463,181	1975	Dulux Australia
Transfer coating resins	Methyl vinyl	W. Germany 2,457,623	1975	Mecanorma Export

Table A.4 (cont.)

Applications	Ethers	Patent	Year	Assignee
Photographic resins	Methyl vinyl	Japan 15,539	1975	Oriental Photo
UV-cured resins and films	Methyl vinyl	Japan 45,075	1975	Agency Industrial Science & Technology
Color diffusion—transfer agent—photographic films	Methyl vinyl	Japan 47,626	1975	Fuji Photo Film
Barrier layer—coatings—photo-graphic films	Methyl vinyl	United States 3,930,859	1976	Bell & Howell
Dye diffusion coatings	Methyl vinyl	France 2,290,698	1976	Eastman Kodak
Radiation-curable resins	Methyl vinyl	Japan 7,365	1977	Upjohn
Coatings	Methyl, ethyl, propyl, etc. vinyl	Japan 10,892	1977	GAF
Photoactive resins—printing plates	Methyl vinyl	Japan 60,882	1977	Kansai Paint
Water-repellent coatings	Methyl vinyl	United States 4,070,152	1978	Ciba-Geigy
Photoactive resins	Vinyloxyethyl cinnamate	Japan 3,430	1978	Nippon Oil Seal
Hair spray formulations	Methyl vinyl	United States 4,164,562	1979	American Cyanamid
Decorative laminate release coatings	>9 Carbon alkyl vinyl	Britain 1,559,655	1979	Formica
Hair dye lacquers	Methyl vinyl	W. Germany 1,645,087	1979	L'Oreal S.A.
Nail polish formulations	Methyl vinyl	W. Germany 2,830,958	1979	Mallinckrodt
Soil-resistant coatings	Methyl vinyl	W. Germany 2,919,886	1979	Unilever S.A.
Radiation-resistant resists	Perfluoroalkyl vinyl	Japan 48,887	1979	Nippon Telegraph and Telephone
Direct-positive silver halide photographic materials	Butyl vinyl	U.S.S.R. 702,337	1979	Belorussian State University
Photosensitive copying coatings	C <sub>2-12</sub> alkyl vinyl	W. Germany 2,834,059	1980	Hoechst A.G.
Parfluoroalkyl ester derivatives for hair spray resins	Methyl vinyl	W. Germany 2,951,922	1980	Daikin Kogyo
Compositions for suppressing plant virus growth	Divinyl	Israel 50,689	1980	Hercules
Photosetting resin compositions	Methyl, propyl, butyl, etc. alkyl vinyl	Japan 33,770	1980	Nippon Oil

Fluorescent screen photosensitive coatings	Methyl vinyl	Japan 34,205	1980	Hitachi KK
Heat-sensitive recording film	Methyl vinyl	Japan 124,697	1980	Mitsubishi Paper
Resist materials	Fluoroalkyl vinyl	Japan 146,446	1980	Nippon Telegraph and Telephone
Video disk coatings	Methyl vinyl	Europe 23,736	1981	Philips Gloeilampen N.V.
Photocurable resins	Methyl vinyl	Japan 8,417	1981	Somar Manufacturing

COMPOSITES

Luminescent binder for glass	Methyl vinyl	W. Germany 1,066,089	1959	General Electric
Nitro paraffin (explosives) binder	Methyl vinyl	United States 3,318,741	1967	Commercial Solvents
Refractory mold (silicates) binder	Methyl vinyl	United States 3,345,302	1967	Philadelphia Quartz
Azide and hydrazine binders—rocket propellant binder	Ethyl vinyl	United States 3,403,062	1968	Dow Chemical
Explosives binder and coatings	Methyl vinyl	United States 3,444,728	1969	American Cyanamid
Nitric acid blasting cap binder	Methyl vinyl	United States 3,447,979	1969	Atlas Chemical
Blasting cap binder resins	Methyl vinyl	United States 3,454,438	1969	American Cyanamid
Electrolytic capacitor binder	Methyl vinyl	United States 3,509,425	1970	General Electric
Mold casting composites	Methyl vinyl	Japan 127,323(4)	1978	Hitachi
Recording material	Methyl vinyl	Japan 124,697	1980	Mitsubishi Paper

CONTROLLED RELEASE POLYMERS

Fertilizer binder	Methyl vinyl	United States 2,652,323	1953	Monsanto
Pesticide dispersant	Methyl vinyl	United States 2,872,369	1959	GAF
I <sub>2</sub> complex for bactericides	Methyl vinyl	Britain 824,215	1959	GAF
I <sub>2</sub> complex bactericide	Methyl vinyl	United States 3,087,853	1963	GAF.
Medicinal coatings	Methyl, ethyl, etc. vinyl	Belgium 622,793	1963	Eli Lilly
Animal antidiarrhea agents	Methyl vinyl	Belgium 644,140	1964	Eli Lilly
Animal antidiarrhea capsules	Methyl, ethyl, etc. vinyl	United States 3,224,941	1965	Eli Lilly
Slow-release medicinal coatings	Methyl vinyl	Netherlands 7,961	1966	Teikoka Hormone Mfg.
Chemical reagent carrier	Methyl vinyl	Netherlands 10,864	1967	Miles Laboratories
Medicinal tablet coatings	Ethyl vinyl	United States 3,407,157	1968	Hoffman-La Roche



Table A.4 (cont.)

Applications	Ethers	Patent	Year	Assignee
Medicinal slow-release carrier	Methyl vinyl	Britain 1,124,115	1968	Fisons Pharmaceuticals
Pharmaceutical microcapsule coatings	Methyl vinyl	France 1,532,740	1968	National Cash Register
Hydrophobic materials capsule coatings—cosmetics, soaps, and lotions	Methyl vinyl	France 1,568,500	1969	T. Kobayashi
Microcapsule coatings	Methyl vinyl	W. Germany 1,903,704	1969	National Cash Register
Fertilizer coatings, slow-release coatings	Methyl vinyl	W. Germany 2,019,724	1970	3M
Placebo tablet coatings, time-release coatings	Methyl vinyl	Britain 1,233,468	1971	Imperial Chemical
Hydrophobic capsule coatings	Methyl vinyl	W. Germany 2,123,861	1971	National Cash Register
Hydrophobic capsule coatings	Methyl vinyl	South Africa 2,853	1971	National Cash Register
Microcapsule—coatings—Hydrophobic liquids	Methyl, ethyl, etc. vinyl	W. Germany 2,133,052	1972	Fuji Photo Film
Controlled-release coatings	C <sub>10-18</sub> alkyl vinyl	United States 3,770,687	1973	GAF
Controlled-release coatings	Methyl vinyl	United States 3,823,025	1974	GAF
Adhesive tape controlled-release coatings	C <sub>10-18</sub> alkyl vinyl	United States 3,855,052	1974	GAF
Medicinal slow-release coatings	Methyl vinyl	France 2,187,290	1974	Purdue Research Foundation
Medicinal controlled-release coatings	Methyl vinyl	W. Germany 2,328,580	1974	Purdue Research Foundation
Encapsulation coatings stabilizer	Methyl vinyl	W. Germany 2,237,843	1974	Phillips G.m.b.H.
Medicinal capsule coatings	Methyl vinyl	United States 3,927,195	1975	Lilly Industries
Water-soluble seed tape binder	Methyl vinyl	France 2,238,416	1975	Canada Wire and Cable
Medicinal controlled-release coatings	Methyl vinyl	United States 4,088,798	1978	Sandoz

COSMETIC ADDITIVES

Cosmetic thickeners	Methyl vinyl	Belgium 629,136	1963	GAF
Steroid carrier cosmetics additive	Methyl vinyl	Belgium 653,150	1965	GAF
Cosmetics dispersants	Methyl vinyl	Belgium 707,487	1968	Oreal A.S.
Cosmetics additives dispersant, emulsifiers	Methyl vinyl	W. Germany 2,530,271	1976	Oreal S.A.
Hair setting agent	Ethyl vinyl	Japan 5,408	1981	Daikin Kogyo

DETERGENT ADDITIVES

Liquid detergent additive	Methyl vinyl	Belgium 624,160	1963	Unilever
Liquid detergent stabilizer	Methyl vinyl	Belgium 637,821	1964	GAF
Liquid detergent stabilizer	Methyl vinyl	United States 3,328,309	1967	GAF
Liquid detergent stabilizer	Methyl vinyl	United States 3,457,342	1969	Monsanto
Thickeners, detergents additives	Methyl, ethyl, propyl, butyl, etc. vinyl	United States 3,499,876	1970	GAF
Laundry detergent dispensing packet films	Methyl vinyl	United States 3,527,197	1970	U.S.D.A.
Detergent builder	Methyl vinyl	United States 3,537,993	1970	Procter & Gamble
Detergent builder	Methyl vinyl	W. Germany 1,959,272	1970	Procter & Gamble
Detergent additive	Methyl vinyl	South Africa 8,951	1970	Procter & Gamble
Polyelectrolyte detergent builders	Methyl vinyl	W. Germany 2,200,140	1972	GAF
Powder detergent emulsifier	Methyl vinyl	W. Germany 2,236,870	1973	Unilever N.V.
Spray dried detergent binder	Methyl vinyl	W. Germany 2,264,302	1973	Unilever N.V.
Detergent builder	Methyl vinyl	United States 3,794,605	1974	Procter & Gamble
Detergent and shampoo viscosity control agent	Methyl vinyl	United States 3,819,540	1974	Gulf Research
Detergent builder	Methyl vinyl	W. Germany 2,243,282	1974	Henkel & Cie
Detergent builder	Methyl vinyl	France 2,237,960	1975	Unilever N.V.
Self-supporting detergent films	Methyl vinyl	W. Germany 2,438,052	1975	Morton-Norwich Products
Textile detergent additive	Methyl vinyl	W. Germany 2,539,071	1976	Henkel & Cie
Textile detergent additive	Methyl vinyl	W. Germany 2,544,035	1976	Henkel & Cie
Low phosphate liquid detergent additive	Methyl vinyl	Europe 1,310	1979	Procter & Gamble

Table A.4 (cont.)

Applications	Ethers	Patent	Year	Assignee
<i>DISPERSANTS/EMULSIFIERS</i>				
Dispersants	Methoxy, ethoxy, etc. butadienes	United States 2,344,085	1944	Eastman Kodak
Emulsifiers	Methyl vinyl	United States 2,479,908	1949	Monsanto
Fire extinguisher foam stabilizers	Methyl vinyl	United States 2,506,062	1950	GAF
Hand cleaner	Methyl vinyl	United States 2,702,277	1955	GAF
Iodine carrier	Methyl vinyl	United States 2,752,281	1956	Rohm & Haas
Latex protective colloid	Methyl vinyl	United States 2,998,400	1956	Wyandotte Chemical
Detergent additives	Methyl, ethyl, etc. vinyl	Britain 872,530	1957	Monsanto
Dispersant protective colloid	Methyl vinyl	Japan 2,995	1957	Mitsubishi Chemical
Silver halide-gelatin stabilizer, photographic films	Methyl vinyl	United States 2,836,769	1958	DuPont
Polymerization dispersant	Methyl vinyl	United States 2,862,913	1958	Monsanto
PVC emulsifiers	Methyl vinyl	United States 2,917,494	1959	Monsanto
Polymerization dispersant	Methyl vinyl	United States 2,957,857	1960	Monsanto
Dispersants	Methyl vinyl	United States 2,979,487	1961	Monsanto
Polymerization emulsifiers	Methyl vinyl	United States 2,998,400	1961	Wyandotte Chemical
Thickener and emulsifiers	Methyl vinyl	Britain 856,320	1961	B.F. Goodrich
Adhesive emulsifier	Methyl vinyl	United States 3,030,343	1962	B.F. Goodrich
Adhesives, dispersants	Methyl vinyl, ethyl vinyl	Britain 906,230	1962	GAF
TiO <sub>2</sub> + Fe <sub>2</sub> O <sub>3</sub> dispersant for polymers	Divinyl	United States 3,085,077	1963	Hercules Powder
Asbestos paper dispersant, binder	Methyl vinyl	United States 3,113,064	1963	GAF
TiO <sub>2</sub> dispersant photographic coatings	Methyl vinyl	Belgium 636,331	1963	Eastman Kodak
Latex polymerization emulsifier	Methyl vinyl	United States 3,138,577	1964	Borden
Liquid detergent dispersant, stabilizer	Methyl vinyl	United States 3,156,655	1964	Lever Brothers
Protective colloid, thickener	Methyl vinyl	Belgium 637,825	1964	GAF
Bleaching agent modifier	Methyl vinyl	Belgium 643,539	1964	Colgate-Palmolive



Ag halide emulsion stabilizers— photographic films	Ethyl vinyl	Belgium 670,369	1966	Kodak
Dispersant for cosmetics and pharmaceuticals	Methyl vinyl	Britain 1,023,895	1966	Plough
Photographic Ag halide emulsifier	Methyl vinyl	Netherlands 17,159	1966	Gevaert–Agfa N.V.
Photographic Ag halide emulsion stabilizer	Methyl, ethyl, etc. vinyl	United States 3,312,554	1967	Eastman Kodak
Photographic Ag halide emulsion additive	Ethyl vinyl	United States 3,370,046	1968	Eastman Kodak
Inorganic pigment dispersant— photographic films	Methyl vinyl	France 1,540,020	1968	Gevaert–Agfa N.V.
Emulsifier—latex polymerization	Methyl vinyl	Japan 25,178	1968	Mitsubishi Petrochemical
Ag halide emulsion stabilizer	Methyl vinyl	W. Germany 1,904,147	1969	Eastman Kodak
Thickeners, emulsifiers	Methyl vinyl	United States 3,531,427	1970	GAF
Cellulose nitrate latex stabilizer	Methyl vinyl	United States 3,535,248	1970	Hercules
Inorganic pigments dispersant— photocopying	Methyl vinyl	Britain 1,178,839	1970	Gevaert–Agfa N.V.
Textile finishes dispersant	Methyl vinyl	W. Germany 1,904,233	1970	Farbenfabriken
Dispersant, thickeners polyamide dyes	Methyl vinyl, isobutyl vinyl	W. Germany 1,928,349	1970	Badische Anilin
TiO <sub>2</sub> retention aid paper coatings	Methyl, ethyl, etc. vinyl	W. Germany 1,948,755	1970	CIBA Ltd.
Adhesives, protective colloids	Isopropenyl, methyl	W. Germany 2,000,751	1970	Lonza
Dispersants	Methyl, ethyl, isobutyl, tridecyl, etc. vinyl	W. Germany 2,014,242	1970	GAF
Liquid detergent emulsifiers	Methyl vinyl	United States 3,591,508	1971	Monsanto
Ag halide peptizer	Methyl vinyl	United States 3,615,624	1971	Eastman Kodak
Detergent promoters	Methyl vinyl	France 2,075,287	1971	Unilever N.V.
Flowable detergents	Methyl vinyl	W. Germany 2,000,790	1971	Procter & Gamble
Detergent stabilizer	Methyl vinyl	W. Germany 2,043,110	1971	Merck G.m.b.H.
Liquid detergent dispersants	Methyl vinyl	W. Germany 2,062,482	1971	Procter & Gamble
Thickeners, fire extinguisher agents	Methyl, ethyl, etc. vinyl	W. Germany 2,113,212	1971	GAF
Binder and stabilizer—photo- graphic materials	Methyl, ethyl, etc. vinyl	W. Germany 2,129,927	1971	Fuji Photo Film

Table A.4 (cont.)

Applications	Ethers	Patent	Year	Assignee
Chlorinating polyolefin protective colloid	Methyl vinyl	Japan 21,887	1971	Osaka Soda
Protective colloids	Methyl vinyl	United States 3,635,752	1972	Monsanto
Cleaning agent additives	Methyl vinyl	United States 3,700,599	1972	Economics Laboratory
Aqueous PVA stabilizer	Methyl vinyl	United States 3,736,311	1973	DuPont
Polyolefin suspension stabilizer	Methyl vinyl	United States 3,759,888	1973	Osaka Soda
Polyurethane resin emulsifier—coatings	Methyl vinyl	Britain 1,310,728	1973	Dunlop Holdings
Soil redeposition inhibitor—detergent additive	Methyl vinyl	W. Germany 2,165,835	1973	Henkel & Cie
Printing paste dispersant—textile paper coatings	Isobutyl vinyl	W. Germany 2,210,284	1973	Badische Anilin
Hair shampoos	Methyl vinyl	W. Germany 2,310,283	1973	Unilever N.V.
Cleaner additive	Methyl vinyl	Netherlands 759	1973	Beisterfeld W. and Co.
Photographic developer solution stabilizer	Methyl vinyl	United States 3,785,824	1974	3M
Latex resin dispersants	Methyl vinyl	United States 3,799,901	1974	Dow Chemical
Polishing and cleaning mixtures	Methyl vinyl	W. Germany 2,417,172	1974	Procter & Gamble
Photographic Ag halide emulsion modifier	Methyl vinyl	Japan 6,916	1974	Fuji Photo Film
Waterborne resin emulsifiers	Methyl vinyl	Japan 11,250	1974	Research Institute for Production Development
Dispersant, viscosity control agent, liquid detergent builder	Methyl vinyl	Netherlands 16,755	1974	Biesterfeld, W. Co.
Liquid photographic developer additive	Octadecyl vinyl	United States 3,869,397	1975	GAF
Liquid photographic developer dispersant	Octadecyl vinyl	United States 3,907,695	1975	A.B. Amidon
Protective colloid, chelating resin, Pb halide photographic mix stabilizer	Methyl vinyl	Britain 1,407,791	1975	Kodak Ltd.

Brightener—nickel plating baths	Methyl, ethyl, etc. vinyl	France 2,262,122	1975	Anciens Etablissements Pascalis
Aerosol foam	Methyl vinyl	W. Germany 1,542,060	1975	Chemische Werke Huels
Foam stabilizers—bath and hair shampoo	Methyl vinyl	W. Germany 2,347,553	1975	Chemische Werke Huels
Aqueous microcapsule stabilizer	Methyl vinyl	W. Germany 2,517,307	1975	Stauffer Chemical
Protective colloid photographic films	Butyl vinyl	Japan 98,330	1975	Ricoh
Nonmigratory resin emulsifiers	Methyl vinyl	United States 3,932,333	1976	Monsanto
Cosmetic additives dispersant, emulsifiers	Methyl vinyl	W. Germany 2,530,271	1976	Oreal S.A.
Emulsion binder—photographic Ag halide emulsions	Methyl, ethyl, butyl, etc. vinyl	United States 4,033,772	1977	GAF
Hair dye carrier	Methyl vinyl	W. Germany 1,617,707	1978	Oreal S.A.
Microcapsule dispersion agent	Methyl vinyl	Japan 125,273	1978	Mitsubishi Paper
Polymer dispersant	Methyl vinyl	W. Germany 2,908,632	1979	Ciba-Geigy
Aqueous I <sub>2</sub> complexes	C <sub>2-4</sub> alkyl vinyl	W. Germany 2,827,827	1980	BASF A.G.
Dispersant for PVC emulsion pro- duction	Methyl vinyl	W. Germany 2,849,087	1980	BASF A.G.
Salt derivatives for textile washing compositions	Methyl vinyl	W. Germany 3,002,710	1980	Senzora B.V.

ELASTOMERS

Polyurethane elastomer modifier	Methyl vinyl	United States 3,426,099	1969	GAF
Elastomers modifier	Methyl vinyl	Britain 1,184,764	1970	Cassella Farbenwerke

ENZYME/MEDICINAL CARRIER

Enzyme binder resin	Methyl vinyl	W. Germany 1,943,490	1970	Monsanto
Enzyme binder resin	Methyl vinyl	W. Germany 1,944,369	1970	Yeda Research
Enzyme binder resin	Methyl vinyl	W. Germany 1,945,748	1970	Monsanto
Enzyme binder resin	Methyl vinyl	W. Germany 1,948,177	1970	Monsanto
Microbiological nutrient media modifier	Methyl vinyl	W. Germany 2,011,366	1970	Union Carbide



Table A.4 (cont.)

Applications	Ethers	Patent	Year	Assignee
Beer clarifier resins	Methyl vinyl	United States 3,597,221	1971	Monsanto
Detergent enzyme carrier	Methyl vinyl	W. Germany 2,008,990	1971	Merck G.m.b.H.
Detergent agglomerating agent, enzyme carrier	Methyl vinyl	United States 3,664,961	1972	Procter & Gamble
Enzyme binder resins	Ethyl, vinyl, divinyl	W. Germany 2,062,818	1972	Merck G.m.b.H.
Enzyme binder resin	Methyl vinyl	W. Germany 2,356,630	1974	Beecham Group
B-Amylase chelating resin	Methyl vinyl	W. Germany 2,418,708	1974	Miles Laboratories
Trypsin enzyme binder	Methyl vinyl	W. Germany 2,432,518	1975	Beecham Group
EPOXY RESIN HARDENER				
Storage stable epoxy curing formulations	C <sub>14</sub> -C <sub>18</sub> alkyl vinyl	Japan 57,600	1979	Matsushita Electric
FIBERS/FABRICS				
Textile coatings	Methyl vinyl	United States 2,127,236	1938	GAF
Textile sizing	Methyl vinyl	United States 2,209,134(5)	1940	I.G. Farben
Fabric finishes	Methyl vinyl	United States 2,607,761	1952	Chattanooga Research
Fabric coatings	Methyl vinyl	United States 2,609,350	1952	GAF
Polymeric dye	Methyl vinyl	United States 2,639,282	1953	Eastman Kodak
Rayon fiber size	Methyl vinyl	United States 2,677,672	1954	Swift
Dye assist agents	Methyl vinyl	United States 2,722,488(9)	1955	GAF
Cellulose fabric dye assist agents	Methyl vinyl	Britain 740,649	1955	British Celanese
Glass fiber dye assist agents	Methyl vinyl	United States 2,744,835	1956	Owens-Corning
Nylon fabric coatings	Methyl vinyl	United States 2,790,734	1957	Sherwin-Williams
Dispersant-fiber sizing agent	Methyl vinyl	Britain 854,987	1957	Farbenwerke Hoechst
Sizing resins, antistatic agents	Methyl, ethyl, etc. vinyl	Britain 795,135	1958	GAF
Textile coatings	Methyl vinyl	United States 2,880,051	1959	Celanese
Textile sizings	Methyl vinyl	United States 2,901,457	1959	GAF
Textile dye assists	Methyl vinyl	Britain 813,908	1959	Celanese
Antistatic fabric coatings	Methyl vinyl	Britain 839,456	1960	Farbenwerke Hoechst

Textile printing paste additive	Methyl vinyl	United States 3,017,377	1962	Sherwin-Williams
Textile sizing resins	Methyl, ethyl, etc. vinyl	United States 3,161,538	1964	GAF
Wool shrink proofing coatings	Methyl vinyl	Belgium 664,664	1965	R.E. Whitfield
Textile soil-repellent coatings	Methyl vinyl	Netherlands 10,041	1967	Deering-Milliken
Pigment carrier resins	Methyl vinyl	Netherlands 10,514	1967	Oreal S.A.
Water-repellent coatings	Tridecyl vinyl	United States 3,410,720	1968	Monsanto
Wash fast textile coatings	Methyl vinyl	France 1,539,679	1968	GAF
Textile fiber modifiers	Methyl vinyl	United States 3,425,969	1969	J.J. Press
Cellulosic sizing resins	Methyl vinyl	United States 3,459,715	1969	Monsanto
Cellulosic fiber binder disposable sanitary products	Methyl vinyl	United States 3,480,016	1969	Çelanece
Electrostatic textile printing powders	Methyl vinyl	Japan 1,462	1969	Dainippon Printing
Textile finishes dispersant	Methyl vinyl	W. Germany 1,904,233	1970	Farbenfabriken
Dispersants, textile sizes	Substituted vinyl alkyl ethers	W. Germany 1,936,761	1970	Agripot S.A.
Water-repellent textile finishes	Methyl vinyl	W. Germany 1,939,828	1970	Geigg A.G.
Cellulose fleece modifier	Isobutyl vinyl	W. Germany 2,049,832	1972	Badische Anilin
Silicone resin dispersant—textile sizing agent	Isobutyl vinyl	W. Germany 2,137,941	1973	Badische Anilin
Printing paste dispersant—textile paper coatings	Isobutyl vinyl	W. Germany 2,210,284	1973	Badische Anilin
Textiles soil release agent	Methyl vinyl	W. Germany 2,231,834	1973	GAF
Soil-repellent finishes polyester fiber	Methyl vinyl	United States 3,843,388	1974	Procter & Gamble
Polyester fiber modifier	Methyl vinyl	W. Germany 2,342,601	1974	GAF
Textile soil release coatings	Methyl vinyl	United States 4,038,027	1977	Bayer Akt
Textile printing pastes	Methyl vinyl	Britain 1,521,533	1978	Imperial Chemical
Polypropylene dye assist additive	>8 Carbon alkyl vinyl	Japan 40,255	1979	Dart Industries

FILMS

Orientated free films	Methyl, hexadecyl vinyl	W. Germany 2,058,048	1971	GAF
Antistatic coatings—photographic films	Butyl vinyl	W. Germany 2,144,286	1972	Fuji Photo Film

Table A.4 (cont.)

Applications	Ethers	Patent	Year	Assignee
Electrophotographic film barrier layer	Methyl vinyl	France 2,231,991	1974	Eastman Kodak
Hydrophilic antistatic film coatings	Methyl vinyl	United States 3,892,575	1975	3M
Gelatin modified primer coatings	Methyl, ethyl, etc. vinyl	W. Germany 2,613,918	1975	Fuji Photo Film
photographic films				
Direct-positive silver halide, photo-graphic materials	Butyl vinyl	U.S.S.R. 702,337	1979	Belorussian State U.
Polymeric films printable layer com-positions	Methyl vinyl	United States 4,202,923	1980	Hoechst A.G.
Resist materials	Perfluoroalkyl vinyl	Japan 146,446	1980	Nippon Telegraph
<i>ION-EXCHANGE RESINS</i>				
Chromatographic disulfide carrier	Ethyl vinyl	U.S.S.R. 687,081	1979	Institute of Heteroorganic Compounds
<i>LAMINATES</i>				
Paper laminate adhesives	Methyl vinyl	United States 3,133,890	1964	Borden
Decorative laminates	Methyl, ethyl, etc. vinyl	France 1,359,496	1964	Henkel & Cie
Nylon-paper laminate adhesive	Methyl vinyl	United States 3,454,419	1969	St. Regis Paper
Laminates	Methyl vinyl	United States 3,498,788	1970	Polaroid
Laminates with silver image	Methyl vinyl	United States 3,581,416	1971	Polaroid
Refractory laminates chemical setting agent	Methyl vinyl	United States 3,894,572	1975	DuPont
<i>LEATHER MODIFIERS</i>				
Leather coatings	n-Butyl vinyl	United States 2,356,879	1944	Eastman Kodak
Leather modifier resins	Methyl vinyl, ethyl vinyl	United States 2,756,837	1956	GAF



Leather coatings	Methyl vinyl	United States 2,768,056	1956	GAF
Coatings, chrome and leather agent	Methyl vinyl, ethyl vinyl	United States 2,745,837	1958	GAF
LITHOGRAPHIC PLATES				
Diazo type plates	Methyl vinyl	United States 2,703,756	1955	GAF
Presensitized printing plates	Methyl vinyl	W. Germany 1,091,433	1955	3M
Printing plate resins	Methyl vinyl	United States 2,772,972	1956	GAF
Diazo type plates	Methyl vinyl	United States 2,971,842	1961	GAF
Diazo type plates	Methyl vinyl	United States 3,046,128	1962	E. Dietzgen
Diazo printing plate coatings	Methyl vinyl	United States 3,130,051	1964	GAF
Diazo printing plate resin	Methyl vinyl	United States 3,149,972	1964	GAF
Diazo printing plate resins	Methyl vinyl	United States 3,228,768	1966	GAF
Lithographic printing plate lacquers	Methyl vinyl	United States 3,276,360	1966	Eastman Kodak
Lithographic printing plate coatings	Methyl vinyl	W. Germany 1,213,437	1966	GAF
Diazo paper coatings	Methyl vinyl	United States 3,316,092	1967	E. Dietzgen
Photosensitive coatings—litho-graphic printing plates	Methyl vinyl	Britain 1,135,082	1968	Algraphy, Ltd.
Photoreactive resins—printing plates	Methyl vinyl	France 2,098,554	1970	Upjohn
Lithographic printing plate coatings	Methyl vinyl	W. Germany 2,100,217	1971	Eastman Kodak
Lithographic plate coatings	Methyl vinyl	United States 3,669,657	1972	Harris Intertype Corp.

MEMBRANES

Modified cellulose membranes	Methyl vinyl	United States 3,498,841	1970	Borden
Electric cell separator membranes	Methyl vinyl	United States 3,519,483(4)	1970	Borden
Semipermeable membranes	Methyl vinyl	Japan 71,782	1979	Toray Industries, Inc.

Table A.4 (cont.)

Applications	Ethers	Patent	Year	Assignee
<i>METAL COMPLEXING/SESQUESTERING RESINS</i>				
Ag recovery resin—photographic emulsions	Butyl vinyl	U.S.S.R. 148,720	1962	S.M. Kazan
Phosphate mine water coagulant	Methyl vinyl	United States 3,130,167	1964	Nalco Chemical
Detergent chelating additive	Methyl vinyl	United States 3,852,213	1974	GAF
Protective colloid chelating resin	Methyl vinyl	Britain 1,407,791	1975	Kodak Ltd.
Pb halide photographic mix stabilizer				
<i>OIL ADDITIVES</i>				
Lube oils	Methyl vinyl	United States 2,677,662	1954	Standard Oil
Lubricating oils	Methyl, ethyl, etc. vinyl	United States 2,698,297(316)	1954	Socony-Vacuum
Lubricating oils	Methyl, ethyl etc. vinyl	United States 2,704,277	1955	Socony-Mobil
Lubricating oils	Methyl vinyl	United States 2,710,283	1955	Standard Oil
Lubricant additives, viscosity index improver, coatings, adhesives	Methyl vinyl	United States 3,425,942	1969	Lubrizol
Lubricating oils	Methyl vinyl	W. Germany 1,941,581	1970	Mobil Oil
Antistatic agents, hydrocarbon fuel additives	Methyl vinyl	United States 3,578,421	1971	Mobil Oil
Viscosity stabilizer	Methyl vinyl	W. Germany 2,053,243	1971	Imperial Chemical
Fuel oil, antistatic agents	Decyl, octadecyl vinyl	W. Germany 2,104,447	1971	Mobil Oil
Diesel fuel additives	Methyl vinyl	United States 3,729,452	1973	Mobil Oil
Conveyor belt lubricants, liquid detergent softener	Methyl vinyl	W. Germany 2,302,367	1973	Beisterfield W. and Co.
Ester derivatives as oil fluidity improvers	Methyl vinyl	W. Germany 2,941,581	1980	Mobil Oil

PLASTICS

Moldings	Methallyl alkyl	United States 2,415,400	1947	U.S. Rubber
Moldings and coatings	Methyl, ethyl, etc. vinyl	United States 2,543,601(602)	1951	Rohm & Haas
Moldings, films, lubricant additives, adhesives	Divinyl	United States 3,320,216	1967	Peninsular Chemresearch
Antistatic coatings—plastics film	Methyl vinyl	Britain 1,066,188	1967	Bexford Ltd.
Polyamide molding resin modifier	Methyl vinyl	United States 3,781,381	1973	Union Carbide
Clear, transparent plastics	Methyl vinyl	W. Germany 2,914,223	1980	Roehm G.m.b.H.

POLYMER ADDITIVES

Water-glass cement	Methyl vinyl	W. Germany 1,057,267	1959	Farbenwerke Hoechst
PVC fiber modifier	Cetyl vinyl	Japan 14,423	1962	Kureha Chemical
Natural rubber stabilizers	Methyl vinyl	United States 3,284,220	1966	Monsanto
Dextrin adhesives modifier	Methyl vinyl	United States 3,366,587	1968	GAF
PVC impact modifier	Methyl, isobutyl, etc. vinyl	W. Germany 2,005,177	1970	Stauffer Chemical
PVC Stabilizers	Methyl vinyl	United States 3,629,205	1971	Stauffer Chemical
Binder and stabilizer—photographic materials	Methyl, ethyl, etc. vinyl	W. Germany 2,129,927	1971	Fuji Photo Film
Photochromic plastics additive	Methyl vinyl	W. Germany 2,232,682	1973	Celfa A.G.
Zinc phosphate coating modifier	Methyl vinyl, cyclohexyl, etc. vinyl	W. Germany 2,248,867	1973	Dulux Australia
Hydrophilic PVC modifier	Methyl vinyl	Japan 7,499	1973	Tokiron Chemical
Additive to strengthen concrete and self-supporting cement	Methyl vinyl	United States 3,839,269	1974	C.W. Comegys
PVA film modifier	Methyl vinyl	Japan 1,649	1974	Ashi Chemical Ind.
Oil well additive, wax crystallization inhibitor	Methyl vinyl	United States 3,879,177	1975	Mobil Oil
Oxidation-reduction carrier	Methyl vinyl	United States 4,065,435	1977	Fuji Photo Film
Soap binder aid	Methyl vinyl	W. Germany 2,835,001	1979	Colgate-Palmolive
Synthetic binder for photographic emulsions	Halogenated alkyl vinyl	Britain 1,565,359	1980	GAF
Agent to prevent crust buildup in evaporating sugar syrups	Methyl vinyl	W. Germany 2,848,779	1980	Keller and Bohacek



Table A.4 (cont.)

Applications	Ethers	Patent	Year	Assignee
<i>PAPER MODIFIERS</i>				
Paper wet-strength additives	Methyl vinyl	United States 2,723,195	1955	Monsanto
Paper coatings	Isobutyl vinyl	United States 2,756,163	1956	GAF
Glassine type papers	Methyl vinyl	Japan 4,591	1958	Mitsubishi
Paper fiber modifier	Methyl vinyl	United States 3,005,745	1961	GAF
Paper sizing resins	Methyl vinyl	United States 3,015,562	1962	GAF
Paper pulp modifier	Methyl vinyl	United States 3,036,950	1962	Burgess Cellulose
Paper sizing resins	Methyl, ethyl, etc. vinyl	Netherlands 12,318	1965	—
Paper sizing resins	Methyl vinyl	United States 3,291,679	1966	Monsanto
Paper sizing resins	Ethyl vinyl	United States 3,382,142	1968	Monsanto
Paper sizing resins	Methyl vinyl	France 1,508,662	1968	Tenneco Chemicals
Transfer copy sheet resins	Methyl vinyl	United States 3,488,207	1970	Plywood-Champion Papers
Pressure-sensitive recording support	Methyl vinyl	France 2,012,741	1970	National Cash Register
Antistatic paper coatings	Methyl vinyl	Japan 32,770	1970	Mitsubishi Paper Mills
Electrophotographic paper coatings	Methyl vinyl	Britain 1,252,630	1971	Mitsubishi Paper Mills
Paper coatings	Methyl, octadecyl vinyl	United States 3,679,623	1972	GAF
Paper opacifying coatings	Methyl vinyl	Britain 1,270,408	1972	Champion Paper
Electrophotographic paper coatings	Octadecyl vinyl	France 2,170,470	1973	National Cash Register
Electrostatic paper coatings	Methyl, ethyl, etc. vinyl	W. Germany 2,237,008	1973	Ricoh
High-gloss paper coatings	Octadecyl vinyl	France 2,190,887	1974	GAF
Paper sizing resins	Methyl vinyl	Japan 21,252	1974	Kansaki Paper
Paper modifier—wet-strength additive	Methyl vinyl	Japan 5,610	1975	Mitsubishi Paper Mills
Thickeners, paper additives	<i>N</i> -Vinylxyethylhydantoin	W. Germany 2,829,307	1979	Ciba-Geigy A.G.

PRINTING INKS

Photochemical copying resins	Methyl vinyl	United States 3,323,917	1967	GAF
Carbonless coated capsules	Methyl vinyl	France 1,565,952	1969	National Cash Register
Microcapsule coatings	Methyl vinyl	United States 3,817,773	1974	National Cash Register
Pressure-sensitive ink coatings	Methyl vinyl	W. Germany 2,529,427	1976	National Cash Register

SEALANTS/CAULKS

Windshield sealants, swimming pool sealants	Methyl vinyl	United States 3,462,516	1969	Phillips Petroleum
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SOIL ADDITIVES

Erosion control agents	Methyl vinyl	United States 2,625,529	1953	Monsanto
Erosion control agents	Methyl vinyl	United States 2,626,936	1953	Monsanto
Dispersants, soil conditioners	Methyl vinyl	United States 2,759,902	1956	GAF

VINYL PLASTISOLS

PVC plastisol modifier—textile coatings	Methyl vinyl	Japan 16,946	1973	Kanegafuchi Ind.
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WATER-SOLUBLE POLYMERS

Thickener and sizing agent	Divinyl	United States 2,640,039	1953	Hawley Products
Waste liquids flocculant	Methyl vinyl	United States 2,687,374	1954	Monsanto
Hydrophilic colloid	Methyl vinyl	United States 2,712,507	1955	National Cash Register
Hydrophilic colloid	Methyl vinyl	United States 2,730,456(7)	1956	National Cash Register
Thickener and emulsifiers	Methyl vinyl	Britain 856,320	1961	B.F. Goodrich
Hydrophilic colloid	Methyl vinyl	United States 3,041,289	1962	National Cash Register
Water thickener	Methyl vinyl	United States 3,070,543	1962	Pam American Petroleum
Well drilling fluid (mud) additive	Divinyl	United States 3,157,599	1964	Hercules Powder
Thickeners	Methyl vinyl	Belgium 669,919	1966	DuPont

Table A.4 (cont.)

Applications	Ethers	Patent	Year	Assignee
Aqueous thickener	Methyl vinyl	United States 3,341,319	1967	Dow Chemical
Potash slurry flocculant	Ethyl vinyl	United States 3,380,784	1968	Northern Gas Products
Oil well drilling fluid additive	Methyl vinyl	France 1,521,143	1968	GAF
Aqueous thickeners, flocculant, liquid detergent stabilizer	Methyl, ethyl, etc. vinyl and divinyl	France 1,527,412	1968	GAF
Drilling fluid additives	Methyl vinyl	United States 3,472,769	1969	Pan American Petroleum
Fluid injection additive—oil recovery resin	Methyl vinyl	United States 3,475,515	1969	Mobil Oil
Thickeners, textile finishes, latex emulsifiers	Methyl, ethyl, etc. vinyl	W. Germany 1,810,057	1969	Imperial Chemical
Thickeners	Ethyl vinyl	United States 3,520,102	1970	Union Carbide
Thickeners, emulsifiers	Methyl vinyl	United States 3,531,427	1970	GAF
Acrylamide grafted for oil recovery	Methyl vinyl	United States 3,543,855	1970	Mobil Oil
Aqueous thickeners	Methyl vinyl	W. Germany 1,904,309	1970	Bayer
Thickening agent	Methyl vinyl	W. Germany 1,930,673	1970	Imperial Chemical
Aqueous thickeners	Methyl vinyl	Britain 1,241,294	1971	Imperial Chemical
Thickening agents	Octadecyl, hexadecyl vinyl	W. Germany 2,107,569	1971	GAF
Thickeners, fire extinguisher agents	Methyl, ethyl, etc. vinyl	W. Germany 2,113,212	1971	GAF
Metal surface aqueous pretreating stabilizers	Methyl vinyl	W. Germany 2,125,963	1971	Balm Paints
Well drilling fluid additives	Methyl, ethyl, etc. vinyl	United States 3,654,164	1972	Petroleum Solids Control Inc.
Flocculation, flotation, drainage aids	Methyl, ethyl, etc. vinyl	United States 3,679,621	1972	Ciba-Geigy
Animal feed additive	Methyl vinyl	France 2,190,374	1972	Imperial Chemical
Aqueous thickeners	Ethyl vinyl	W. Germany 2,126,472	1972	Imperial Chemical
Sulfomethylated oil recovery resins, thickening agents	Methyl vinyl	United States 3,734,187	1973	Marathon Oil
Inorganic acid solution thickener	Methyl vinyl	United States 3,781,203	1973	GAF
Thickening agents	Methyl, ethyl, hexadecyl, octadecyl, tetradecyl vinyl	Britain 1,329,033	1973	GAF



Drilling mud additives	Methyl vinyl	France 2,183,838	1974	Monsanto
Waste water flocculant	Methyl vinyl	W. Germany 2,414,521	1974	Hitachi
Oil well additive—wax crystallization inhibitor	Methyl vinyl	United States 3,897,177	1975	Mobil Oil
Aqueous redox polymers—H <sub>2</sub> O <sub>2</sub> production aid	Methyl vinyl	W. Germany 2,460,677	1975	Fuji Photo Film
Water-soluble thickeners	Methyl, ethyl, etc. vinyl	W. Germany 1,795,676	1978	GAF
Oil well additives	Methyl vinyl	United States 4,169,818	1979	Celanese

TUMOR INHIBITOR—MEDICINAL

Tumor inhibitor	Divinyl	United States 3,244,943	1965	Hercules Powder
Pathogenic foot and mouth disease suppressant	Methyl vinyl	United States 3,624,218	1971	Hercules
Animal cholesterol reducer agent	Methyl vinyl	France 2,074,603	1971	Monsanto
Antiviral suppressants	Divinyl	United States 3,749,771	1973	Hercules
Animal tumor inhibitor	Divinyl	United States 3,794,622	1974	Hercules
Pathogenic herpes simplex virus suppressant	Divinyl	United States 3,812,248	1974	Hercules
Animals virus growth suppressant	Divinyl	United States 3,859,433	1975	Hercules
interferon production stimulant				

Table A.5. Vinyl Acetate–Maleic Anhydride Copolymer Patents

Applications	Patent	Year	Assignee
<i>PRODUCTION PROCEDURE</i>			
Production procedure for granular polymer	United States 2,522,775	1950	DuPont
Vinyl formate copolymer production	United States 2,562,853	1951	Monsanto
Production procedure	Italy 601,428	1960	Montecantini
Production procedure	W. Germany 2,031,507	1971	Economics Laboratory
Copolymer production	Romania 62,698	1977	Combinatul Petrochimic
<i>ADHESIVES</i>			
Adhesives and coatings	United States 2,637,712	1953	National Starch Products
Adhesive resins base	Japan 2,291	1958	Arakawa Forest Products Chemical
Pressure-sensitive adhesives	United States 2,876,895	1959	U.S.D.A.
Remoistenable paper adhesives	United States 2,917,396	1959	Dennison Mfg.
Adhesives and coating resins	France 1,400,133	1965	Badische Anilin
Adhesives for wood and plastics	Britain 1,052,843	1966	Arakawa Forest Chemicals Ind.
Pressure-sensitive adhesive resins	Netherlands 6,854	1966	Beiersdorf Co.
Flame-resistant paper laminate adhesives	United States 3,305,431	1967	Swift & Co.
Epoxy crosslinker for coatings and adhesives	United States 3,422,076	1969	American Cyanamid
Fully esterified product for medical bandage adhesives	Japan 25,589	1969	Tanable Seyaka
Glycidyl methacrylate modified for postage stamp adhesives	Japan 5,399	1970	Arakawa Forest Chemical Ind.
Gum tape adhesives	Japan 12,638	1971	Kao Soap
Aluminum–paper laminate adhesives	Japan 17,440	1971	Hekisto Gosei
Salt derivative as mortar cement and tile adhesive additive to improve strength	Japan 18,038	1971	Shin-Etsu Chemical Ind.
Adhesives	Romania 53,132	1972	Combinatul Petrochimic
Starch modifier for adhesives	Japan 10,377	1973	Daicell

Table A.5 (cont.)

Applications	Patent	Year	Assignee
Ester derivatives for poly- ester film adhesives	United States 4,084,035	1978	Rhone-Poulenc
Adhesive for polyolefin- metal sheets	W. Germany 1,934,434	1978	Mitsubishi
Adhesives for polyolefin- metal sheets	Japan 19,629	1978	Mitsubishi
Waterborne hot melt fabric adhesives	Japan 76,635	1979	Nippon Synthetic Chemical
Hot melt adhesives	Japan 139,945	1979	Nippon Synthetic Chemical

*BOILER SCALE CONTROL AGENT*

Acid form for boiler scale removal agent	United States 2,723,956	1955	National Aluminate
Polyelectrolyte for boiler scale removal	United States 3,715,307	1973	Economics Laboratory
Boiler scale inhibitor poly- electrolytes	United States 3,755,264	1973	Amicon
Water treatment agents, detergent additives, boiler scale remover agents	W. Germany 2,405,192	1974	Ciba-Geigy

*COATINGS*

Adhesives and coatings	United States 2,637,712	1953	National Starch Products
Antistatic coatings for photographic film	United States 2,647,836	1953	DuPont
Coating pigment binder	W. Germany 879,019	1953	Farbwerke Hoechst
Fertilizer coatings and binder	United States 2,703,276	1955	Monsanto
Lacquer coating resins for photographic light filters	United States 2,801,188	1957	Eastman Kodak
Lactone derivative for photographic film base backing or stripping material	United States 2,861,056	1958	Eastman Kodak
Mineral fines dust pallatives	United States 2,894,851	1959	American Cyanamid
Protective coating formula- tions	Belgium 584,365	1959	Kodak
Photographic film coatings	Japan 8,245	1960	Fuji Photo Film
Photographic film coatings	Japan 13,092	1960	Fuji Photo Film
Binder resin for photosensi- tive coatings	United States 2,990,281	1961	Monsanto



Table A.5 (cont.)

Applications	Patent	Year	Assignee
Lactone derivatives for photographic film stripping layer	United States 3,007,901	1961	Eastman Kodak
Polyolefin film coatings	Britain 913,476	1962	International Development Co.
Water-soluble paint resins	Japan 1,474	1962	Kanegafuchi Spinning
Galvanic cell anode film layers	United States 3,092,518	1963	Union Carbide
Flexible, protective antihalation coatings for photographic films	United States 3,102,028	1963	Eastman Kodak
Coatings for photographic films	Belgium 630,170	1963	Agfa A.G.
Photographic film coating formulations	W. Germany 1,166,616	1964	Adox Fotowerke
Cinnamoyl derivative for photographic coatings and films—photoactive coatings	Japan 17,063	1964	Fuji Photo Film
Adhesives and coatings resins	France 1,400,133	1965	Badische Anilin
Alkali-soluble lactones for photographic film coatings	United States 3,260,706	1966	Eastman Kodak
Hair waving formulation resins	Netherlands 658	1966	Oreal S.A.
Crosslinked phosphorus containing resins for coatings	United States 3,303,042	1967	Westinghouse Electric
Pigment carrier resins	Netherlands 10,514	1967	Oreal S.A.
Vinyl butyrate resin for anti-friction coatings	U.S.S.R. 203,813	1967	State Scientific Research Institute
Photographic film coatings	Britain 1,114,799	1968	DuPont
Back coatings for photographic film supports	France 1,539,752	1968	Fuji Photo Film
Traffic marker coatings	United States 3,450,556	1969	Union Shoe Machinery
Photographic film image layer top coatings	Britain 1,150,499	1969	Fuji Photo Films
Photoactive resins	France 1,555,957	1969	GAF
Amide derivatives for photographic film stripping layers	France 1,585,064	1970	Fuji Photo Film
Crosslinking agent for photographic emulsion coatings	W. Germany 1,809,606	1970	Agfa-Gevaert A.G.
Salt-hydrazide derivatives for plastics antistatic coatings	Britain 1,222,154	1971	Konishiroku Photo Ind.
Imide derivatives as antistatic coatings for photographic films	W. Germany 2,011,649	1971	Agfa-Gevaert A.G.
Photographic film coatings	W. Germany 2,040,389	1971	Fuji Photo Film

Table A.5 (cont.)

Applications	Patent	Year	Assignee
Support coatings for photo-graphic layers	W. Germany 2,058,236	1971	Fuji Photo Film
Plastics antistatic coatings	W. Germany 2,116,258	1971	Fuji Photo Film
Antistatic coatings for photo-graphic film	United States 3,634,336	1972	Eastman Kodak
Derivatives for radiation curable resins	United States 3,703,402	1972	General Electric
Electrophotographic recording plate coatings	France 2,101,392	1972	Eastman Kodak
Binder for photographic film coatings	W. Germany 2,202,479	1972	Fuji Photo Film
Hydrophilic interlayer coating for printing plates	W. Germany 1,309,511	1973	Fuji Photo Film
Vinyl laurate copolymer for photographic film, antihalation layers, and antistatic coatings	W. Germany 1,422,810	1973	DuPont
Derivatives for glass bottle coatings	W. Germany 2,309,777	1973	Dart Industries
Flame-resistant coatings binder	Japan 16,701	1973	Asahi Chemical Ind.
Support resins for light sensitive photographic materials	United States 3,811,913	1974	Fuji Photo Film
Amide derivatives as coatings emulsifiers	W. Germany 1,595,704	1974	Bayer A.G.
Coatings for photographic films	W. Germany 2,344,785	1974	Fuji Photo Film
Copper acetate treated (crosslinked) coatings	Japan 93,471	1974	Japan Synthetic Rubber
Salt derivatives for electroconductive receptor side coatings	United States 3,876,463	1975	Eastman Kodak
Resin with pendent oxidation-reduction groups	United States 4,065,435	1977	Fuji Photo Film
Ester derivative production	Britain 1,467,130	1977	Rhone-Poulenc Ind.
Photographic film subbing layer coatings	United States 4,120,724	1978	Fuji Photo Film
Dispersant for latex coatings	United States 4,228,047	1980	Air Products

COMPOSITES

Antiagglomerating agent for urea-formaldehyde resins	United States 3,554,947	1971	Kao Soap
Binder for bitumen insulation	W. Germany 2,012,465	1971	Teroson-Werke G.m.b.H.
Salt derivative as binder for abrading compositions	Japan 7,441	1974	Kao Soap

Table A.5 (cont.)

Applications	Patent	Year	Assignee
<i>CONTROLLED RELEASE POLYMERS</i>			
Binder for pest control chemicals	Switzerland 266, 274	1950	CIBA, Ltd.
Fertilizer coatings and binder	United States 2,703,276	1955	Monsanto
Iron slow-release coatings	Netherlands 7,961	1966	Teikoku Hormone Mfg.
Colloid for microencapsulation process	Japan 12,472	1978	Fuji Photo Film
<i>DETERGENT ADDITIVES</i>			
Detergent additives	Britain 872,530	1957	Monsanto
Detergent builder resins	W. Germany 1,961,959	1970	Economics Laboratory
Detergent additives	South Africa 8,951	1970	Procter and Gamble
Cleaning formulations additive	United States 3,700,599	1972	Economics Laboratory
Detergent builder resins	W. Germany 2,307,775	1973	ICI America
Amide salts for washing solution builders	Britain 1,361,641	1974	Chemische Werke Huels
Detergent builder and stabilizer	W. Germany 2,243,282	1974	Henkel and Cie
Water treatment agents, detergent additives, boiler scale remover agents	W. Germany 2,405,192	1974	Ciba-Geigy
Hydrolyzed copolymer in dishwashing detergents	Canada 980,209	1975	Nalco Chemical
<i>DISPERSANTS/EMULSIFIERS</i>			
Dispersant for polymerization of vinyl esters	United States 2,486,855	1949	Shawiningan Resins
Amide derivatives as dispersants for photographic Ag halide emulsions	United States 2,522,042	1950	GAF
Emulsifiers for polystyrene production	United States 2,545,702	1951	Monsanto
Thickeners, sizes, and protective colloids	United States 2,640,039	1953	Hawley Products
Dispersant for photographic emulsions	Japan 6,523	1953	Mitsubishi Paper
Dispersant for PVC production	United States 2,772,257	1956	Monsanto
Dispersant for aminoplast bead preparation	Britain 755,147	1956	Monsanto
Saponified resin as dispersant for PVC production	Japan 7,540	1956	Kanegafuchi Chemical Ind.



Table A.5 (cont.)

Applications	Patent	Year	Assignee
Hydrophilic dispersant for Ag halide photographic emulsions	Belgium 551,312	1957	Gevaert Photo Producten
Emulsifiers for PVC production	United States 2,917,494	1959	Monsanto
Dispersant for PVC production	Japan 445	1959	Nippon Carbide
Emulsifier for PVC production	United States 2,957,857	1960	Monsanto
Dispersant for PVC production	Italy 601,428	1960	Montecantini
Dispersant for polystyrene production	Britain 887,356	1962	Vinyl Products, Ltd.
Photographic emulsion stabilizer	W. Germany 1,136,110	1962	Gevaert Photo Producten
Amide-salt derivatives as silica dispersants for pre-coating diazo materials	United States 3,163,535	1964	GAF
PVC production emulsifiers	Belgium 637,626	1964	Societa Edison S.p.A.
Dispersant for PVC production	Britain 1,052,871	1966	Societa Edison S.p.A.
Ag halide photographic	Netherlands 17,159	1966	Gevaert-Agfa
Latex coating emulsifiers	France 1,511,183	1968	Monsanto
Inorganic pigment dispersants	France 1,540,020	1968	Gevaert-Agfa
Dispersants for PVC production	Japan 26,307	1968	Toyo Koatsu Ind.
Dispersant for PVA and poly(vinyl propionate) or poly(vinyl pivalate) production	W. Germany 1,292,857	1969	Badische Anilin
Inorganic pigment dispersants	Britain 1,178,839	1970	Gevaert-Agfa
Ester derivatives for latex emulsifiers	E. Germany 77,066	1970	E. Anton
Dispersants for aqueous metal dispersions and viscosity control agent	United States 3,607,218	1971	Fuji Photo Film
Dispersant for Ag halide photographic emulsions and antihalation layers	W. Germany 1,447,770	1973	Agfa A.G.
Photographic development solution dispersants	United States 3,785,824	1974	3M
Dispersants for latex coatings	United States 3,799,901	1974	Dow Chemical
PVC dispersant and production aid	France 2,186,485	1974	Shin-Etsu Chemical

Table A.5 (cont.)

Applications	Patent	Year	Assignee
Dispersant for aluminum hydroxide paper coatings	Japan 27,507	1974	Kanzaki Paper
Ester derivatives for styrene-olefin copolymer dispersions	Japan 141,693	1975	Denki Kagaku Kogyo
Nonmigratory latex emulsifiers	United States 3,932,333	1976	Monsanto
Antiplating dispersant or stabilizer for olefin-maleic anhydride copolymer production	United States 3,933,763	1976	Nalco Chemical
Dispersant for PVC production	Belgium 847,631	1977	Nissan Chemical Ind.
Dispersant for PVA production	Japan 91,039	1977	Kuraray
Complexing agent for water softening	Japan 22,549	1978	Consort Electrochem. Ind.
Dispersant for PVC emulsion production	United States 4,182,819	1980	Wacker Chemie G.m.b.H.
Dispersant for latex coatings	United States 4,228,047	1980	Air Products
Flocculant and protective colloid resin	Romania 73,876	1980	Petru Poni Institute

ENZYME/MEDICINAL CARRIER

Enzyme binder resins	W. Germany 1,943,490	1970	Monsanto
Enzyme binder resins	W. Germany 1,944,369	1970	Yeda Research
Enzyme binder resins	W. Germany 1,945,748	1970	Monsanto
Soluble resin carrier for enzymes	W. Germany 1,948,177	1970	Monsanto

EPOXY RESIN HARDENERS

Modifier-hardener for epoxy castings	W. Germany 1,100,113	1961	Westinghouse Electric
Epoxy crosslinker for coatings and adhesives	United States 3,422,076	1969	American Cyanamid

FIBERS/FABRICS

Perfluoresters in textile coatings	United States 2,580,504	1952	Purdue Research Foundation
Epoxide derivatives for textile coatings	United States 2,607,761	1952	Chattanooga Research Foundation
Derivatives for nylon yarn sizing	United States 2,686,137	1953	Monsanto

Table A.5 (cont.)

Applications	Patent	Year	Assignee
Nylon sizing resins	United States 2,808,348	1957	Monsanto
Nylon sizing resins	Britain 783,672	1957	Monsanto
Salt derivatives for textile emulsion coatings	Britain 889,103	1962	Kanegafuchi Spinning Co.
Wool textile creasing agents	Netherlands 2,090	1966	Oreal S.A.
Ester derivatives for textile soil release coatings	United States 3,563,795	1971	Monsanto
Ammonium salt for polyester fiber sizing	France 2,064,114	1971	Electro Chemical Ind.
Water-repellent polyester textile coatings	Japan 31,838	1971	Toyo Spinning
Water-repellent polyester textile coatings	Japan 31,839	1971	Toyo Spinning
Protective colloid for glass fibers	United States 3,635,752	1972	Monsanto
Salt derivatives for textile sizing agents	Japan 611	1972	Omi Keneshi Spinning
Ammonium salt derivatives for antistatic, soil-release textile coatings	Japan 49,480	1972	Kanebo
Wool shrinkproofing coatings	W. Germany 2,305,216	1973	Sumitomo
<i>FILMS</i>			
Flexible, protective antihalation coatings for photographic films	United States 3,102,028	1963	Eastman Kodak
Coatings for photographic films	Belgium 630,170	1963	Agfa A.G.
Photographic film coating formulations	W. Germany 1,166,616	1964	Adox Fotowerke
Alkali-soluble lactones for photographic film coatings	United States 3,260,706	1966	Eastman Kodak
Polymeric binders for photographic films	France 1,467,686	1967	Eastman Kodak
Antihalation layers for films	W. Germany 1,254,016	1967	Adox Fotowerke
Photographic film coatings	Britain 1,114,799	1968	Dupont
Back coatings for photographic film supports	France 1,539,752	1968	Fuji Photo Film
Imide derivatives as anti-static coatings for photographic films	W. Germany 2,011,649	1971	Agfa-Gevaert
Photographic film coatings	W. Germany 2,040,389	1971	Fuji Photo Film
Support coatings for photographic layers	W. Germany 2,058,236	1971	Fuji Photo Film
Antistatic coatings for photographic film	United States 3,634,336	1972	Eastman Kodak



Table A.5 (cont.)

Applications	Patent	Year	Assignee
Binder for photographic film coatings	W. Germany 2,202,479	1972	Fuji Photo Film
Coatings for photographic films	W. Germany 2,344,785	1974	Fuji Photo Film
Photographic film subbing layer coatings	United States 4,120,724	1978	Fuji Photo Film
<i>ION-EXCHANGE RESINS</i>			
Hydrolysis and lactonized product for cation-exchange resins	Japan 2,936	1968	Arakawa Forest Chemical Ind.
<i>LAMINATES</i>			
Thermosetting laminating resins	United States 2,519,764	1950	DuPont
Laminating resins	Japan 77,485	1975	Mitsui Petrochemical
<i>LEATHER MODIFIERS</i>			
Amide derivatives for leather dyeing	Netherlands 6,540	1966	Farbenfabriken Bayer
Synthetic leather additives	W. Germany 2,101,158	1972	State Research Institute Kozedelny
<i>LITHOGRAPHIC PLATES</i>			
Photosensitive printing plate resins	W. Germany 2,251,030	1973	Fuji Photo Film
<i>MEMBRANES</i>			
Ester derivatives for semi-permeable membranes	United States 3,877,978	1975	U.S. Dept. Interior
<i>METAL COMPLEXING/SEQUESTERING RESINS</i>			
Beer clarifier agent	United States 3,597,221	1971	Monsanto
Heavy-metal recovery resins	Japan 38,880	1973	—
Complexing agent for water softening	Japan 22,549	1978	Consort Electrochemical Ind.
<i>OIL ADDITIVES</i>			
Pour point depressants	United States 2,616,849	1952	Socony-Vacuum
Ester derivatives as viscosity index improvers	United States 2,616,851	1952	Socony-Vacuum

Table A.5 (cont.)

Applications	Patent	Year	Assignee
Viscosity index improver	United States 2,616,853	1952	Socony-Vacuum
Ester derivatives for oil viscosity index control	United States 2,698,316	1954	Socony-Vacuum
Ester derivatives for oil additives	Britain 921,124	1963	Esso Research
Ester derivatives as viscosity index improver	W. Germany 1,145,290	1963	Esso Research
Lubricating oil additives, viscosity index modifier	Britain 1,638,228	1966	Esso Research
Behenyl ester as pour point depressant	W. Germany 1,941,581	1970	Mobil Oil
Alcohol and amide derivatives for oil viscosity control	United States 3,637,610	1972	Esso Research
<i>PLASTICS</i>			
Aminoplast binder and modifier for moldings	United States 2,838,468	1958	Monsanto
<i>PAPER MODIFIER</i>			
Lead derivative—PVC additive to improve electrical properties	United States 2,483,959	1949	Monsanto
Modifier for polyacrylonitrile fiber production	United States 2,575,006	1951	Monsanto
Aminoplast binder and modifier for moldings	United States 2,838,468	1958	Monsanto
Colored thermoplastic film	Japan 2,496	1962	Fuji Photo Film
Colored films and plastics	Japan 20,498	1963	Fuji Photo Film
Melamine-formaldehyde resin modifier	W. Germany 1,910,472	1970	Farbenwerke Hoechst
Antiagglomerating agent for urea-formaldehyde resins	United States 3,554,947	1971	Kao Soap
Salt-hydrazide derivatives for plastics antistatic coatings	Britain 1,222,154	1971	Konishiroku Photo Ind.
Amide derivatives for foam-cement formulations	Japan 16,519	1971	Omi Kenshi Spinning Co.
Soap bar binding additive	W. Germany 2,835,001	1978	Colgate-Palmolive
Crosslinked paper sizing materials	Japan 18,336	1967	Arakawa Forest Chemical Ind.
Electrophotographic paper coatings	Britain 1,252,630	1971	Mitsubishi Paper Mills

Table A.5 (cont.)

Applications	Patent	Year	Assignee
Paper modifier for improved strength	Japan 401	1971	Japan Synthetic Chemical Ind.
Electrostatic paper coatings	W. Germany 2,237,008	1973	Ricoh
Dispersant for aluminum hydroxide paper coatings	Japan 27,507	1974	Kanzaki Paper
Saponified resins for paper sizing materials	Japan 9,882	1975	Nippon Synthetic Chemical Ind.
Paper sizing resins	Japan 88,306	1979	Nippon Synthetic Chemical
Ester derivatives for paper coatings	Japan 22,054	1980	Nippon Synthetic Chemical
Water absorption resins, paper sizing agent	Japan 99,925	1980	Nippon Synthetic Chemical
<i>PRINTING INKS</i>			
Colloid transfer print layer process resins	Belgium 636,329	1963	Gevaert Photo Producten N.V.
<i>SEALANTS/CAULKS</i>			
Concrete sealants formulations	Belgium 665,347	1965	Bergwerksverband G.m.b.H.
Sealants for construction materials	Netherlands 6,780	1966	Bergwerksverband G.m.b.H.
<i>SAND BINDER</i>			
Sand binder resins for metal castings	W. Germany 1,189,677	1965	Monsanto
<i>WATER-SOLUBLE POLYMERS</i>			
Thickeners, sizes and protective colloids	United States 2,640,039	1953	Hawley Products
Water clarification flocculants	Belgium 528,842	1953	Union Chimique Belge S.A.
Polyelectrolyte for decolorization of aqueous solutions, wines, and oils	Italy 512,407	1955	Montecantini
Polyelectrolyte flocculants	Italy 527,269	1955	Montecantini
Hydrolyzed copolymer for clay flocculation additive	Italy 577,302	1958	Palibento S.r.L.
Polyelectrolyte crystallization promoter for salts	Britain 822,893	1959	Palmer, Mann & Co.
Clay flocculant for low solids drilling fluids	United States 3,070,543	1962	Pan American Petroleum



Table A.5 (cont.)

Applications	Patent	Year	Assignee
Water-soluble paint resins	Japan 1,474	1962	Kanegafuchi Spinning
Flocculants for photo-graphic Ag halide emulsions	W. Germany 1,145,485	1963	Perutz Photowerke G.m.b.H.
Drilling mud flocculants	United States 3,297,569	1967	Pan American Petroleum
Clay beneficiating resins for well drilling operations	United States 3,360,461	1967	Pan American Petroleum
Cr derivatives for polyester photographic films coatings	France 1,465,452	1967	Fuji Photo Film
Crosslinked with vinyl crotonate for aqueous thickening agents	Japan 20,779	1967	Arakawa Forest Chemical Ind.
Flocculants for waste water inorganic solids	United States 3,492,225	1970	Nalco Chemical
Aqueous thickeners	Britain 1,241,294	1971	Imperial Chemical
Glycol modifier for moldable gels	Japan 8,860	1973	Japan Synthetic Chemical Ind.
Betonite clay modifier for drilling muds	United States 3,838,047	1974	Monsanto
Bentonite clay modifier for drilling muds	France 2,183,838	1974	Monsanto
Flow control agents	United States 3,912,670	1975	O'Brien Corp.

Table A.6. Patents on Maleic Anhydride Copolymers with Miscellaneous Monomers

Applications	Monomers	Patent	Year	Assignee
PRODUCTION PROCEDURE				
Production procedure, coatings	Vinyl acetophenone	United States 2,713,570	1955	Eastman Kodak
Production procedure	Vinyl $\beta$ , $\beta$ -dimethyl acrylate	France 1,105,938	1955	Société d'électrochimie
Production procedure	2-Vinyl-1,3-dioxane	Japan 40,054	1970	Asahi Chemical
Production procedure	Phenylacetylene	U.S.S.R. 219,193	1970	Institute of Chemistry and Physics
Production procedure, coatings	Allyl acetate	W. Germany 2,228,107	1973	Electrochemische Industrie
Production procedure	Vinyl trialkoxysilanes	Belgium 866,525	1978	Dynamit Nobel
Coatings—production procedure	Vinyl trialkoxysilanes	W. Germany 2,719,458	1978	Dynamit Nobel
High quality resins	Vinyl trialkoxysilanes	Britain 1,586,650	1981	Dynamit Nobel
Low molecular weight polyanhydrides	$\alpha$ -Methylstyrene	W. Germany 2,149,584	1981	Plaskon Products
ADHESIVES				
Adhesives, coatings, and moldings	2-Allyloxyacetic acid, 3-allyloxypropionic acid, and 4-allyloxybutyric acid	United States 2,602,786	1952	Swift & Co.
Glass fiber adhesives	Dimethallyl ether	United States 2,611,718	1952	Owens-Corning Fiberglass
Films, fibers, and paper adhesives	$\beta$ -Methylene-b-propiolactone	United States 2,653,146	1953	DuPont
Coatings, adhesives	2-Vinyloxyethyl glycidyl ether	United States 3,000,690	1958	Rohm & Haas
Coatings, adhesives	3-Methylene-cyclobutane-carbonitrile	United States 2,914,541	1959	DuPont
Soil conditioners, coatings, adhesives resins	Diallyl barbituric acid	United States 3,057,829	1962	3M
Adhesives for vinyls	N-Propyl-N-vinyl acetamide	Britain 1,031,444	1966	Monsanto
Coatings, adhesives	Vinyl cyclohexene monoxide	U.S.S.R. 178,105	1966	Scientific Research Inst.
Epoxy resin hardeners, improved adhesives for glass	Triethoxy vinylsilane	France 1,572,851	1969	Shin-Etsu Chemical

Adhesives, coating formulations	<i>N</i> -(1,3-Diphenyl-1-methyl-3-oxypropyl) acrylamide	United States 3,578,637	1971	Lubrizon
Rubber adhesion promoter	$\alpha$ -Pinene	W. Germany 1,694,829	1972	Reichhold-Albert-Chemie
Coatings, adhesives	Glycidyl allyl ether of ethylene glycol	U.S.S.R. 408,953	1973	Irkutsk State University
Metal coatings, adhesives	Vinyl silanes	Belgium 855,370	1977	Dynamit Nobel
Water-soluble adhesives	<i>N</i> -Vinyl-2-pyrrolidone	Japan 33,926	1977	Nitto Electric Ind.
Adhesives, coatings, and filtration aids	Vinyl trialkoxysilanes	W. Germany 2,730,008	1979	Dynamit Nobel
Hardener for epoxy resins	Acetamidoethylene	United States 4,260,714	1981	Dynapol

BOILER SCALE CONTROL AGENT

Boiler scale remover	Acrylic acid	United States 3,755,264	1973	Amicon
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CELLULAR MATERIALS

Crosslinked cellular materials	2-Vinyl or 4-isopropenyl-phenoxyacetic acid	United States 2,850,465	1958	Koppers
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COATINGS

Laminates, coatings	2-Methyl-4-methylene-1,3-dioxalene, 2,3-dimethyl-4-methylene-1,3-dioxalane, 2-phenyl-4-methylene-1,3-dioxalone	United States 2,382,640	1945	Eastman Kodak
Coatings	2-Chloroallyl acetate	Britain 576,022	1946	Eastman Kodak
Coatings	Ethyl methallyl ether	United States 2,415,400	1947	U.S. Rubber
Moldings, coatings, and films	2-Methyl and 2-phenyl-4-methylene, 1,3-dioxalane, 2-methylene-1,4-dioxaspiro[4.5]decane	United States 2,415,638	1947	Eastman Kodak



Table A.6 (cont.)

Applications	Monomers	Patent	Year	Assignee
Molding resins, films, and lacquers	1-Acetoxy, 1-propionoxy or 1-isobutyroxy-1, 3-butadiene	United States 2,432,460	1947	Eastman Kodak
Molding resins, films, and coatings	1-Acetoxy-1,3 butadiene	Britain 584,622	1947	Eastman Kodak
Coatings, cation-exchange resins	Vinyl thioacetate	Britain 585,755	1947	Imperial Chemical
Dielectric materials	3-Vinylphenoxathine	United States 2,449,528	1948	General Electric
Coatings	Allyl or methallyl- <i>o</i> -benzoyl benzoate	United States 2,461,301	1949	U.S. Rubber
Coatings, impregnating layers	Allyl caproate, sterate, laurate, myristate, and levulinate	United States 2,533,376	1950	Libby-Owens-Ford
Dielectric coatings	3-Vinylphenoxxythine	Britain 644,677	1950	Thomson-Houston
Coatings	$\alpha$ -Methylstyrene	United States 2,561,313	1951	Monsanto
Thermosetting resins	Vinyl formate	United States 2,562,853	1951	Monsanto
Glass coatings	Allyl and methallyl triethoxysilane, diallyl diethoxysilane, triallyl ethoxysilane	Britain 663,770	1951	Libby-Owens-Ford
Surface active agents	$\beta$ -Methylene- $\beta$ -propiolactone	United States 2,585,537	1952	DuPont
Adhesives, coatings, and moldings	2-Allyloxyacetic acid, 3-allyloxypropionic acid, and 4-allyloxybutyric acid	United States 2,602,786	1952	Swift & Co.
Glass coatings	Allyl and methallyl triethoxysilanes	United States 2,632,755	1952	Libby-Owens-Ford
General purpose coatings	Allyl rosinate	United States 2,639,273	1952	Hercules
Production procedure—coatings	Vinyl acetophenone	United States 2,713,570	1955	Eastman Kodak
Coatings, films, molding resins	<i>N</i> -Vinyl- <i>N</i> -methyl benzamide	United States 2,717,886	1955	Monsanto
Glass coatings	Alkenyl triethoxysilanes	United States 2,728,785	1955	DuPont
Photography dye coupler resins	1 or 6-Methoxy-2-vinyl-naphthalene	United States 2,739,956	1956	Eastman Kodak
Coatings	2-Vinylphenoxy acetamide, 4-vinylphenoxy acetamide, 4-isopropenylphenoxy acetamide	United States 2,811,507	1957	Koppers
Coatings	Vinyl senecioate	Britain 786,391	1957	Electrochemical Society Ugine

Moldings, coating laminates, ion-exchange resins	2-(4-allylphenoxy)-1-chloroethane	United States 2,827,442	1958	Koppers
Thermosetting resin blends with epoxy resins	3-Allyl or 4-allyl phenoxy acetamide	United States 2,850,482	1958	Koppers
Derivatives for light sensitive printing plates	Vinyl toluene	United States 2,861,058	1958	Eastman Kodak
Coating and laminating resins	1-Methyl-3-methylene-cyclobutene, 1-methyl-3-isopropylidene-cyclobutene or 1,4,4-trimethyl-3-methylenecyclobutene	United States 2,995,543	1958	DuPont
Coatings, adhesives	2-Vinyloxyethyl glycidyl ether	United States 3,000,690	1958	Rohm & Haas
Coatings, adhesives	3-Methylene-cyclobutane-carbonitrile	United States 2,914,541	1959	DuPont
Thermoset resins	Allyl chloride	Belgium 576,837	1959	Société Solvay
Moldings and protective coatings	N-Carbaminylmaleimide	W. Germany 1,100,288	1959	U.S. Rubber
Varnish and impregnating resins	Indene	W. Germany 1,110,416	1961	Bergwerksverband G.m.b.H.
Metal coatings	Vinyl phosphonic acid	Belgium 614,785	1962	Farbwerke Hoechst A.G.
Color photography resins	1-Hydroxy-N-( $\beta$ -vinyloxyethyl)-naphthamide	Belgium 618,202	1962	DuPont
Self-polishing floor and car waxes	Vinyl sterate	Britain 950,766	1964	Air Reduction
Waxes and molding resins	Trimethylolpropane allyl ether	France 1,359,586	1964	Celanese Corp.
Coatings	Indene, coumarone	W. Germany 1,161,026	1964	F. A. Henglein
Thermosetting resins with epoxies	Monallyl phthalate	Japan 544	1965	Japan Catalytic
Concrete waterproofing coatings	Indene	Britain 1,044,696	1966	Bergwerksverband G.m.b.H.
Coatings, adhesives	Vinyl cyclohexene monoxide	U.S.S.R. 178,105	1966	Scientific Research Inst.
Coatings	Allyl phenyl ether, 1,3,5-trichlorophenyl allyl ether	Japan 20,776	1967	Nippon Kagaku
Photoreactive resins	p-Vinyl acetophenone, p-isopropenyl-acetophenone	U.S.S.R. 197,169	1967	Institute of High Molecular Weight Compounds
Coatings	Itaconic acid	Belgium 716,565	1968	Oreal S.A.
Nail polish resins	Itaconic acid	Belgium 718,865	1969	Oreal S.A.

Table A.6 (cont.)

Applications	Monomers	Patent	Year	Assignee
Molding resins coatings, electrical insulating resins	Meta or <i>para</i> -isopropenyl-phenyl-dimethyl-carbinol	France 1,574,376	1969	Farbenfabriken Bayer A.G.
Hair setting agents	Itaconic anhydride, methacrylic acid	W. Germany 1,929,103	1969	Oreal S.A.
Coatings	4-Vinyl-2-azetidinone	W. Germany 1,805,045	1960	Farbwerke Hoechst
Electroconductive coatings	<i>N</i> -Vinylpyrrolidone	W. Germany 2,003,191	1970	Agfa-Gevaert
Photoconductive resins	2-Methyl- <i>N</i> -vinyl indole, 3-methyl- <i>N</i> -vinyl indole	United States 3,554,741	1971	IBM
Adhesives, coating formulations	<i>N</i> -(1,3-Diphenyl-1-methyl-3-oxypropyl) acrylamide	United States 3,578,637	1971	Lubrizol
Coatings	Phenanthrene	Japan 3,061	1971	Research Institute Production Development
Antistatic plastics coatings	Vinyl triethoxy silane	Japan 13,825	1971	Shin-Etsu Chemical
Coatings	Allyl chloride	Japan 29,495	1971	Osaka Soda
Thixotropic coatings	Methallyl alcohol	W. Germany 1,595,159	1972	Progil
Water-soluble coatings	Allyl alcohol, methallyl alcohol	W. Germany 2,058,879	1972	Farbenfabriken Bayer A.G.
Antihalation layer and antistatic coatings for photographic films	Vinyl laurate	W. Germany 1,422,810	1973	DuPont
Production procedure, coatings	Allyl acetate	W. Germany 2,228,107	1973	Electrochemische Industrie
Corrosion-resistant steel coatings	Vinylphosphonic acid	Japan 8,700	1973	Nippon Steel
Coatings, adhesives	Glycidyl allyl ether of ethylene glycol	U.S.S.R. 408,953	1973	Irkutsk State University
Photoconductor resins	9-( <i>p</i> -Vinylphenyl) anthracene	Japan 74,945	1974	Hitachi
Photoreactive resins	Vinyl benzyl cinnamate	Japan 99,589	1974	Fuji Photo Film
Photocurable resins	Methyl vinyl ether	France 2,253,772	1975	Quadrimental Offset
Photosensitive resins for resists	$\beta$ -Vinylloxyethyl cinnamate	Japan 60,218	1975	Nippon Oil Seal Ind.
Linear, self-crossing resins	<i>p</i> -Isopropenylphenyl glycidyl ether	U.S.S.R. 478,026	1975	Institute Petrochemical Process
Coatings, crosslinking agent	Allyl acetate	Japan 48,679	1976	Consont Elektrochem



Metal coatings, adhesives	Vinyl silanes	Belgium 855,370	1977	Dynamit Nobel
Polyelectrolytes, coatings	Allyl acetate	W. Germany 2,228,107	1977	Consort Elektrochem
Thermosetting resins	3-(2-Vinylphenoxy)-ethanol	United States 2,850,480	1978	Koppers
Thermosetting resins	3-(2-Vinylphenoxy) propanol, 1-(2-vinylphenoxy) propanol, 2-(4-isopropenyl phenoxy) propanol	United States 2,850,481	1978	Koppers
Coatings-production procedure	Vinyl trialkoxysilanes	W. Germany 2,719,458	1978	Dynamit Nobel
Adhesives, coatings and filtration aids	Vinyl trialkoxysilanes	W. Germany 2,730,008	1979	Dynamit Nobel
Calcium carbonate powder coating	Acrylic acid	Japan 45,699	1979	Shiraishi Kogyo
Linear, self-crosslinking resins	2-Glycidoxymethyl-1-vinylcyclopropanes	U.S.S.R. 757,545	1980	Institute Petrochemical Processes
Aqueous copolymers for coatings	Vinyl silanes	Britain 1,584,633	1981	Dynamit Nobel
Aqueous copolymers for coatings	Vinyl silanes	Britain 1,584,634	1981	Dynamit Nobel

CONTROLLED RELEASE POLYMERS

Resins with fungicidal properties	Allyl ether of 2,4 dichlorophenol and 2,4,6-trichlorophenol	United States 2,497,927	1950	Rohm & Haas
Water-soluble estradiol binder	N-Vinylpyrrolidone	France 1,342,168	1963	Takeda Chemical Ind.
Tablet coating resins	Methyl- <i>n</i> -vinyl-5-carboxy-2-pyrrolidone, methyl <i>n</i> -allyl-pyroglyutamate	Netherlands 4,878	1965	Merck & Co.
Therapeutic agent carrier	N-Vinylpyrrolidone	U.S.S.R. 373,278	1973	Institute High Molecular Weight Compounds

COSMETIC ADDITIVES

Crosslinked resins	Indene	Britain 1,558,328	1979	Standard Oil
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DETERGENT ADDITIVES

Biodegradable detergent builder	Methyl isobutyl ketone	Netherlands 5,685	1972	Shell
Detergent builder	1-Butene-2,3,4-tricarboxylic acid	United States 3,717,616	1973	FMC

Table A.6 (cont.)

Applications	Monomers	Patent	Year	Assignee
Detergent builder	2-Chloroacrylic acid	W. Germany 2,212,623	1973	Knapsack A.G.
Detergent builders	2-Methyl-2-propene sulfonate	W. Germany 2,221,735	1973	Chemische Werke Huels
Detergent builders	p-Vinylphenol	Japan 21,403	1974	Maruzen Oil
Detergent builders	Monoallyl maleate, monoallyl fumarate	United States 3,865,793	1975	Milchem, Inc.
Detergent builders	Acrylic acid	W. Germany 2,349,643	1975	Hoechst A.G.
Detergent builders	Vinyl sulfonic acid, methallyl-sulfonic acid	Japan 149,705	1975	Lion Fat and Oil
Detergent builders	Acrylic acid	Japan 140,986	1976	Nippon Shokubai Kagaku Kogyo
DISPERSANTS/EMULSIFIERS				
Surface active agents	$\beta$ -Methylene- $\beta$ -propiolactone	United States 2,585,537	1952	DuPont
Emulsifier for photographic solutions	Vinyl hydroquinone	United States 2,694,693	1954	Eastman Kodak
Latex pigment dispersant	N-Vinyl-4-methyl-2-oxazolidinone	United States 3,044,992	1962	Dow Chemical
Photographic emulsion dispersant	N-Vinylpyrrolidene	W. Germany 1,123,913	1962	Agfa A.G.
Dispersant for silicates	N-Vinyl-5-methyl-2-oxazolidinone	United States 3,179,171	1965	Dow Chemical
Salts for polymeric dispersants	N-Vinyl-4-methyloxazolidinone	United States 3,324,063	1967	Dow Chemical
Dispersants	p-Vinylbenzoic acid	U.S.S.R. 208,261	1967	Institute of High Molecular Weight Compounds
Dispersants	p-Vinylbenzoic acid	U.S.S.R. 208,263	1967	Institute of High Molecular Weight Compounds
Dispersants	Acrylamide	Britain 1,129,196	1968	Cassella Farbwerke Mainkur
Coating dispersants	4-Vinyl-5-methyl-m-dioxane, 2-vinyl 5-(chloromethyl)-m-dioxane-5-methanol, 2-vinyl-1,3-dioxolane-4-methanol	Japan 34,148	1970	Asahi Chemical

Foam inhibitor for water hydro-carbon systems	Vinyl sterate	United States 3,730,894	1973	Mobil Oil
Ag halide dispersant for photographic emulsions	Dialkyl derivatives of 1,3-dihydroxy-2-methylene-propane	United States 3,926,635	1975	Agfa-Gevaert
Ag halide dispersant for photographic emulsions	Dialkyl derivatives of 1,3-dihydroxy-2-methylene-propane	W. Germany 2,332,562	1975	Agfa-Gevaert
Surfactants, fogging inhibitor for glass	Diketene	Japan 8,870	1977	Ciba-Geigy
Dispersant, paper sizing, thickeners, floor polish additives	Norbornene-2,3-dicarboxylic acid anhydride	Britain 1,512,572	1978	Borg-Warner
Sodium salt-scale inhibitor for desalination units	Allylsulfonic acid	Europe 9,304	1980	American Cyanamid
Binder resin for photographic silver halide emulsions	N-Vinylpyrrolidone	Britain 1,565,359	1980	GAF
Dispersants for aqueous suspensions	Vinyl trialkoxy silanes	Britain 2,026,006	1980	Dynamit Nobel
Dispersant for polymer emulsions	Vinyl trialkoxy silanes	United States 4,267,093	1981	Dynamit Nobel
Calcium carbonate dispersant	Acrylic acid	Britain 1,585,448	1981	Kao Soap

EPOXY RESIN HARDENERS

Thermosetting resin blends with epoxy resins	3-Allyl or 4-allylphenoxy acetamide	United States 2,850,482	1958	Koppers
Thermosetting resins with epoxies	Monallyl phthalate	Japan 544	1965	Japan Catalytic
Epoxy resin hardener improved adhesives for glass	Triethoxy vinylsilane	France 1,572,851	1969	Shin-Etsu Chemical
Epoxy resin hardener	Vinyl triethoxy silane	Japan 4,068	1971	Shin-Etsu chemical
Epoxy resin curative	$\alpha$ -Methylstyrene	W. Germany 2,149,583	1972	Allied Chemical
Epoxy resin hardener	$\alpha$ -Methylstyrene	United States, 3,929,738	1975	Allied Chemical
Epoxy resin hardener, water-soluble resins	2,5-Dihydrofuran	United States 4,011,282	1977	Chevron Research
Encapsulate epoxy resin hardener	$\alpha$ -Methylstyrene	France 2,398,779	1979	Allied Chemical
Epoxy resin hardeners	Isopropenyl alkylbenzene	Japan 98,175	1980	Sumitomo Chemical



Table A.6 (cont.)

Applications	Monomers	Patent	Year	Assignee
<i>FIBERS/FABRICS</i>				
Textile and paper sizing, leather tanning agents	10-Hendecenoic acid	United States 2,510,902	1950	Hercules
Esters for plasticizers, textile sizing agents	2-Chloromethylallyl chloride	United States 2,571,883	1951	Hercules
Fiber dye assist resins	5-Ethyl-2-vinylpyridine	Italy 545,417	1956	Montecatini
Wool shrinkproofing coatings	2-Vinyloxyethyl glycidyl ether, 2-vinyl-thioethyl glycidyl ether, 5-vinyl-oxypentyl glycidyl ether	United States 2,949,474	1960	Rohm & Haas
Polymeric dyes	1-[ <i>n</i> -( $\beta$ -Vinyloxyethyl) benzene sulfonamide]-3-methyl-5-benzoxypyrazole	Britain 995,363	1965	DuPont
Textile fiber dye assist agents	<i>N</i> -Vinyl-5-methyl-2-oxazolidinone	United States 3,328,357	1967	Dow Chemical
Chromium complexes—water-repellant finishes	Vinyl silane esters	United States 3,692,747	1972	Nalco Chemical
Textile finishing agent, water-repellant coatings	Allyl or methallyl perfluoroisopropyl ether	W. Germany 2,208,020	1972	A. G. Pittman
Fabric coatings	Heptafluoroisopropyl methallyl ether	United States 3,706,594	1973	U.S.D.A.
Oil and water-repellent coatings for textiles	Heptafluoroisopropyl methallyl ether	United States 3,901,998	1975	U.S.D.A.
Textile coatings	Heptafluoroisopropyl methallyl ether	United States 4,029,867	1977	U.S. Sec. Agriculture
<i>FILMS</i>				
Moldings, coatings, and films	2-Methyl and 2-phenyl-4-methylene 1,3-dioxalane, 2-methylene-1,4-dioxaspiro[4,5]decane	United States 2,415,638	1947	Eastman Kodak

Molding resins, films, and coatings Films	1-Acetoxyl-1,3 butadiene <i>p</i> -Vinylbenzoic acid	Britain 584,622 U.S.S.R. 245,975	1947 1969	Eastman Kodak Institute of High Molecular Weight Com- pounds DuPont
Antihalation layer and antistatic coatings for photographic films	Vinyl laurate	W. Germany 1,422,810	1973	

ION-EXCHANGE RESINS

Coatings, cation-exchange resins Cation-exchange resins	Vinyl thioacetate Allyl acetate	Britain 585,755 Britain 727,476	1947 1955	Imperial Chemical Chemische Fabrik Budenheim
Ion exchange resin, surgical jellies	Sucrose allyl ethers	United States 2,798,053	1957	B. F. Goodrich
Moldings, coating laminates, ion- exchange resins	2-(4-Allylphenoxy)-1-chloroethane	United States 2,827,442	1958	Koppers
Ion-exchange resins, soil con- ditioners	Dimethallyl	United States 2,955,994	1960	Esso Research
Coagulant, ion-exchange, and chelate resins	<i>p</i> -Vinylphenol	Japan 22,187	1973	Maruzen Oil
Ion-exchange resins	3-(Chloromethyl)-3-(allyloxymethyl)-Japan oxetane	56,776	1973	Research Institute Product Development
Copolymer salt pastes hydrophilic filler	Phenyl vinyl ether Divinyl benzene	U.S.S.R. 450,820 W. Germany 2,433,486	1974 1975	— S. Hudecek
Coagulants and ion-exchange resins	Vinylphenols	Japan 16,995	1979	Maruzen Oil

LAMINATES

Laminates, coatings	2-Methyl-4-methylene-1-3- dioxalene, 2,2-dimethyl-4- methylene-1,3-dioxalane, 2- phenyl-4-methylene-1,3- dioxalone	United States 2,382,640	1945	Eastman Kodak
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Table A.6 (cont.)

Applications	Monomers	Patent	Year	Assignee
Glass bonding adhesives, laminates	2,2-Bis(4-allylcarbonate-3,5-dichlorophenyl) propane	United States 2,587,442	1952	B. F. Goodrich
Glass cloth laminates	Allyl citrates	Britain 952,228	1964	Miles Laboratory
Casting resins, laminates	2-Vinyl-1,3-dioxane-5-methyl-5-carbinol, 2-vinyl-1,3-dioxane-5-ol, 2-vinyl-1,3-dioxolan-4-carbinol	United States 3,433,773	1969	Asahi Chemical
Plasticizers, laminating resins	2-Phenylallyl acetate or alcohol	United States 3,511,820	1970	Sinclair Research
LEATHER MODIFIERS				
Textile and paper sizing, leather tanning agents	10-Hendecenoic acid	United States 2,510,902	1950	Hercules
LITHOGRAPHIC PLATES				
Resist printing plates	Acrylic acid	Japan 40,597	1973	Kanebo
MEMBRANES				
Asbestos coatings, impregnating resins	Divinyl benzene	W. Germany 1,160,422	1964	PPG
Membranes	Acrylic acid	U.S.S.R. 449,918	1974	All-Union Scientific Research Institute
METAL COMPLEXING/SEQUESTERING RESINS				
Heavy-metal extracting resins	Diketene	United States 2,722,481	1955	DuPont
Salts as metal sequestering agents	N-Vinyl-5-methyl 2-oxazolidinone	United States 3,328,358	1967	Dow Chemical
Chromium complexes—water-repellant finishes	Vinyl silane esters	United States 3,692,747	1972	Nalco Chemical



Coagulant, ion-exchange, and chelate resins	<i>p</i> -Vinylphenol	Japan 22,187	1973	Maruzen Oil
Metals complexing agent	Allyl acetate			
Ca <sup>2+</sup> sequestering agent	<i>N</i> -Vinylindole, <i>N</i> -vinylpyrrole	W. Germany 2,238,375	1974	Electrochemische Industrie
Cationic heavy-metal trapping resins—chelating resins	Thiophene	W. Germany 2,514,760	1975	SNAM Progetti S.p.A.
		Japan 145,377	1975	Physical Research Institute
Metal chelating resins	Vinyl butyl sulfide	U.S.S.R. 765,285	1980	Irkut University

OIL ADDITIVES

Ester derivatives as oil additives	Thiophene	United States 2,540,794	1951	Socony–Vacuum
Pour point depressants	Butadiene monoxide	United States 2,582,708	1952	Standard Oil Develop.
Viscosity index improver	Allyl benzoate	United States 2,615,864	1952	Socony–Vacuum Oil
Esters as pour point depressants	Allyl laurate and sterate	United States 2,616,852(3)	1952	Socony–Vacuum Oil
Oil additives	Allyl laurate	United States 2,698,298	1954	Socony–Vacuum
Lube oils	Allyl tetradecyl ether	United States 2,704,277	1955	Socony–Vacuum Oil
Lubricating oils	Allyl sterate	W. Germany 945,282	1956	Socony Mobil Oil
Viscosity index improvers	<i>N</i> -(1,3-Diphenyl-1-methyl- <i>e</i> -oxopropyl) acrylamide	United States 3,425,942	1969	Lubrizol

PLASTICS

Moldings, coatings, and films	2-Methyl and 2-phenyl-4-methylene 1,3-dioxalane, 2-methylane-1,4-dioxaspiro[4.5]decane	United States 2,415,638	1947	Eastman Kodak
Castings, moldings	2,5-Dichlorostyrene	United States 2,578,259	1951	U.S. Sec. Navy
Castings and laminates	Diallylimido carbonate	United States 2,708,189	1955	U.S. Rubber
Coatings, films, molding resins	<i>N</i> -Vinyl- <i>N</i> -methyl benzamide	United States 2,717,886	1955	Monsanto
Coating and laminating resins	1-Methyl-3-methylene cyclobutene, 1-methyl-3-isopropylidene cyclobutene or 1,4,4-trimethyl-3-methylene cyclobutene	United States 2,995,543	1958	DuPont
Waxes and molding resins	Trimethylolpropane allyl ether	France 1,359,586	1964	Celanese Corp.

Table A.6 (cont.)

Applications	Monomers	Patent	Year	Assignee
<i>POLYMER ADDITIVES</i>				
Esters for plasticizers, textile sizing agent	2-Chloromethylallyl chloride	United States 2,571,883	1951	Hercules
Esters for plasticizers	2,3-Dichloropropene	United States 2,719,836	1955	GAF
Salt derivatives for setting time control in Portland cements	<i>N</i> -Vinyl-2-oxazinidinone, <i>N</i> -vinyl-2-oxazolidinone, <i>N</i> -vinyl-5-methyl-2-oxazolidinone, <i>N</i> -vinyl-4-ethyl-2-oxazolidinone	United States 3,116,264	1963	Dow Chemical
Aluminous cement modifiers	<i>N</i> -Vinyl-morpholine, <i>N</i> -vinyl-pyrrolidone, <i>N</i> -vinyl-2-oxazinidinone, <i>N</i> -vinyl-2-oxazolidinone	United States 3,140,269	1964	Dow Chemical
Plasticizers, laminating resins	2-Phenylallyl acetate or alcohol	United States 3,511,820	1970	Sinclair Research
Rubber adhesion promoter	$\alpha$ -Pinene	W. Germany 1,694,829	1972	Reichhold-Albert-Chemie
Peroxide containing resins, initiators	Vinyl propynyl peroxides	U.S.S.R. 454,217	1974	Lvov Polytechnik Institute
Coatings, crosslinking agent	Allyl acetate	Japan 48,679	1976	Consort Elektrochem
Flame retardant for potting, molding, and casting compounds	2,3,4,6-Tetrachloro <i>m</i> -xylylene-glycol bisallyl ether	United States 4,031,163	1977	Dynamit Nobel
Fireproofing additive for polycarbonates	Na allylsulfonate	Japan 50,064	1979	Teijin Chemicals
<i>PAPER MODIFIERS</i>				
Textile and paper sizing, leather tanning agents	10-Hendacanoic acid	United States 2,510,902	1950	Hercules
Paper sizing agents	Allyl sterate	United States 3,427,219 (3,428,485)	1969	Monsanto
Dispersant, paper sizing, thickeners, floor polish additives	Norbornene-2,3-dicarboxylic acid anhydride	Britain 1,512,572	1978	Borg-Warner

Paper sizing agent  
Calcium carbonate dispersant for paper sizing

$\alpha$ -Methylstyrene  
Acrylic acid

E. Germany 142,217  
Britain 1,585,448

1980  
1981

VEB Leuna-Werk  
Kao Soap

SEALANTS/CAULKS

Construction sealants

Indene

Netherlands 6,780

1966  
Bergwerksverband  
G.m.b.H.

SOIL ADDITIVES

Soil structure modifier, water-repellent textile finishes

N-Vinyl lactams

United States 2,676,949

1954  
Monsanto

Ion-exchange resins, soil conditioners

Dimethallyl ether

United States 2,955,994

1960  
Esso Research

Soil conditioners, coatings, adhesives resins

Diallyl barbituric acid

United States 3,057,829

1962  
3M

Flocculants, soil conditioners

N-Vinyl-2-methyl imidazole, 2-vinylpyridine

United States 3,634,366

1972  
Daicell

Soil sealing compositions

Acrylamide

United States 3,772,893

1973  
Dow Chemical

WATER-SOLUBLE POLYMERS

Aqueous thickeners for basic dyes  
Polymeric hydroperoxides  
Additives to thin drilling muds

Isopropenyl acetate  
p-Isopropyl- $\alpha$ -methylstyrene  
N-Vinyl-morpholine, N-vinyl-pyrrolidone, N-vinyl-2-oxazinedione, N-vinyl-2-oxazolidinone

United States 2,452,165  
United States 2,911,391  
United States 3,108,956

1948  
1959  
1963  
Eastman Kodak  
Hercules  
Dow Chemical

Salt derivatives for setting time control in Portland cements

N-Vinyl-2-oxazinidinone, N-vinyl-2-oxazolidinone, N-vinyl-5-methyl-2-oxazolidinone, N-vinyl-4-ethyl-2-oxazolidinone

United States 3,116,264

1963  
Dow Chemical



Table A.6 (cont.)

Applications	Monomers	Patent	Year	Assignee
Aluminous cement modifiers	<i>N</i> -Vinyl-morpholine, <i>N</i> -vinyl-pyrrolidone, <i>N</i> -vinyl-2-oxazinidinone, <i>N</i> -vinyl-2-oxazolidinone	United States 3,140,269	1964	Dow Chemical
Oil recovery resin—hydrocarbonaceous dispersant	<i>N</i> -Vinyl-2-oxazolidinone	United States 3,244,188	1966	Dow Chemical
Polyelectrolytes	2,3-Bis(diethylphosphono)-1,3-butadiene	U.S.S.R. 280,844	1970	Institute of Organic & Physical Chemistry
Thickeners for aqueous solutions	2-Methyl-4-(vinylloxymethyl)-1,3-dioxolane	Britain 1,223,015	1971	British Oxygen
Flocculants, soil conditioners	1-Vinyl-2-methylimidazole, 2-vinylpyridine	United States 3,634,366	1972	Daicell
Foam inhibitors—oil well drilling mud additives	Vinyl sterate	France 2,126,525	1972	Mobil Oil
Water-soluble coatings	Allyl alcohol, methallyl alcohol	United States 3,876,588	1975	Bayer A.G.
Epoxy resin hardener, water-soluble resins	2,5-Dihydrofuran	United States 4,011,282	1977	Chevron Research
Polyelectrolytes, coatings	Allyl acetate	W. Germany 2,228,107	1977	Consort Elektrochem
Coagulants and ion-exchange resins	Vinylphenols	Japan 16,995	1979	Maruzen Oil
<i>TUMOR INHIBITOR—MEDICINAL</i>				
Antitumor active copolymers	1,3-Propanediol, 2-methylene diacetate	W. Germany 2,740,081	1979	Bayer A.G.

Table A.7. MA Graft Polymer Patents

Applications	Substrate	Patent	Year	Assignee
ADHESIVES				
Elastomers and textile adhesives	Rubber	United States 2,844,502	1958	U.S. Rubber
General purpose	Petroleum resins	United States 3,005,800	1961	P. O. Powers
Cellulosics	Polyethylene	Belgium 625,908	1963	Union Carbide
Polyolefins	Polyethylene	Belgium 636,783	1963	Union Carbide
Polyolefins with adhesion promoters	Polypropylene	Belgium 652,324	1965	Hercules
Adhesion promoters	Polypropylene	Belgium 659,184	1965	Hercules
General purpose	Polyether acetate	Belgium 673,274	1966	Cassella Farbwerke
General purpose	Polyethylene	Poland 51,836	1966	Politechnika Warszawska
Improved adhesives	Polyethylene	Poland 52,067	1966	Politechnika Warszawska
Polyester and epoxy resin hardeners	Poly(vinyl alkyl ether)	Britain 1,059,255	1967	Cassella Farbwerke
Polyolefins	Polyethylene	Britain 1,059,973	1967	Union Carbide
Resin production	Propylene oxide-co-butadiene monoxide polymer	United States 3,398,126	1968	Allied Chemical
Metal and plastics adhesion promoters	Polyethylene and ethylene-co-propylene polymer	Britain 1,101,408	1968	Hercules
Textiles	Polypropylene and propylene-co-1-butene	France 1,516,084	1968	Eastman Kodak
Al-paper laminates	Polypropylene, poly(propylene-co-1-butene), poly(propylene-co-pentene), and polybutene	United States 3,433,777	1969	Eastman Kodak
Caulks	Styrene-co-isobutylene polymer	United States 3,438,950	1969	Esso Research
Polyolefin-aluminum laminates	Hydrocarbon polymers	United States 3,450,560	1969	Chevron Research
General purpose	Degraded HMW poly ( $\alpha$ -olefins)	United States 3,481,910	1969	Eastman Kodak
Emulsions for textiles	Polyethylene	Britain 1,141,943	1969	Eastman Kodak
Rubber modifier	Petroleum resin	France 1,576,333	1969	Japan Oil
Hot melt	Polyethylene	W. Germany 1,928,553	1969	Eastman Kodak

Table A.7 (cont.)

Applications	Substrate	Patent	Year	Assignee
General purpose	Polybutadiene (>80% <i>cis</i> -1,4)	W. Germany 1,929,593	1970	Vianova Kunsthartz
General purpose	Styrene-co-maleic anhydride	W. Germany 1,945,835	1970	Shell
General purpose	Hydrocarbon waxes	W. Germany 1,946,357	1970	Dunlop Co.
Rubber bonding	Styrene-co-butadiene latex	Japan 8,341	1970	Toyo Rubber
Specialty	Polypropylene	Japan 32,356	1970	Chisso Corp.
Epoxy resin hardener	Polybutadiene	Japan 39,182	1970	Japan Soda
Paper	Petroleum resins	W. Germany 2,001,511	1971	—
Polyolefin-metal	Polyethylene	W. Germany 2,020,901	1971	Continental Can Company
Vinyl ether-co-maleic anhydride grafted polyolefins	1,2 and 1,4-polybutadiene and polybutadiene	W. Germany 2,105,528	1971	Kansai Paint
General purpose	$\alpha$ -Olefin terpolymers	U.S.S.R. 299,514	1971	—
Hot melt	Polyethylene	United States 3,658,948	1972	Eastman Kodak
Acrylics-maleic anhydride grafts	Glass fabric	United States 3,698,931	1972	Polymer Research Corp.
Grafting procedures adhesives	1,2-Polybutadiene	W. Germany 2,147,639	1972	Kansai Paint
Glass fiber	Polypropylene	W. Germany 2,226,059	1972	Imperial Chemical
General purpose	Poly(vinyl acetate)	Romania 53,132	1972	Combinatul Petrochimic
Hot melt	H.D. Polyethylene	Romania 54,317	1972	Combinatul Petrochimic
Epoxy resin hardener	Poly(ethylene-co-vinyl acetate)	United States 3,760,031	1973	Asahi Chemical
General purpose	Epichlorohydrin-ethylene oxide copolymer	France 2,146,995	1973	Hercules
Acrylic ester-co-maleic anhydride grafted	Ethylene-co-vinyl acetate polymer	W. Germany 2,147,318	1973	Toyo Soda
Hot melt	Isotactic polypropylene	W. Germany 2,244,684	1973	Sumitomo Chemical
Ethylene-propylene-diene rubber	Polybutadiene	W. Germany 2,326,198	1973	Revertex Ltd.
General purpose	Ethylene-vinyl acetate copolymers	Japan 37,130	1973	Asahi Chemical
General purpose resins	Butadiene-co-cyclopentadiene polymer	Britain 1,356,309	1974	Esso Research
Polyolefin-Al foil	Ethylene-co-vinyl acetate polymer	W. Germany 2,329,780	1974	Toyo Soda
Acrylates-co-maleic anhydride grafted-hot melt adhesives	Polypropylene	W. Germany 2,350,331	1974	Toyo Soda



Specialty	Petroleum resins	W. Germany 2,364,169	1974	Societa Italiana
Alt. ethylene-co-maleic anhydride grafts—hot melt adhesives	Polyethylene	W. Germany 2,415,987	1974	DuPont
Neoprene rubber	Petroleum resins	W. Germany 2,416,443	1974	Nippon Oil
General purpose	1,3-Polypentadiene	Japan 28,694	1974	Japan Zeon
Specialty	Polyolefins	Japan 96,094	1974	—
Pressure sensitive	<i>cis</i> -1,4-Polyisoprene	Japan 97,060	1974	Kuraray Co.
Epoxy resin hardener	Liquid polybutadiene (>60% <i>cis</i> 1,4)	Japan 100,122	1974	Nippon Zeon
Transparent tapes	20:80 Poly(cyclopentene-co-1,3-pentadiene)	Japan 108,141	1974	Nippon Zeon
Hot melt	Polypropylene	Japan 109,432	1974	Toa Nonryo Kogyo
Specialty	Poly(ethylene-co-butadiene)	Japan 122,591	1974	Mitsui Petrochemical Ind.
Alt. styrene-co-maleic anhydride grafted polyolefins	Polyolefin waxes	United States 3,883,458	1975	BASF A.G.
General purpose	Ethylene-co-butadiene polymer (mostly <i>trans</i> -1,4-)	W. Germany 2,434,668	1975	Mitsui Petrochemical Ind.
Epoxy curing agent	Polybutadiene	W. Germany 2,513,123	1975	French Petroleum Institute
General purpose	Polyisobutylene	W. Germany 2,523,692	1975	Rhone-Poulenc S.A.
Hot melt	HD Polyethylene	Japan 4,144	1975	Mitsui Petrochemical Ind.
Polyolefin adhesion promoter for laminates	Polypropylene	Japan 4,167	1975	Mitsubishi Petrochemical
Metal laminates	Polypropylene	Japan 15,874	1975	Mitsui Petrochemical Ind.
Polyolefins	Polypropylene	Japan 34,075	1975	Sumitomo Chemical Co.
Hot melt	Styrene-co-butadiene	Japan 56,427	1975	Asahi Chemical Ind.
Adhesion promoter for polyolefin-polyamides	Polypropylene	Japan 59,458	1975	Mitsubishi Rayon Co.
Wood	1,2-Polybutadiene	Japan 76,148	1975	Matsushita Electric Works
Hot melt	Molten polyolefin	Japan 119,888	1975	—
Vinyl monomers + maleic anhydride graft—metal adhesives	Ethylene-co-vinyl acetate polymer	Japan 5,390	1976	Toyo Soda
Plywood	Polybutadienes	Japan 10,845	1976	Sumitomo Chem.
Rosin substitute	1,3-Pentadiene polymers	Japan 127,193	1976	Nippon Zeon
Specialty	High mol. wt. 1,2-polybutadiene	Britain 1,493,185	1977	Japan Synthetic

Table A.7 (cont.)

Applications	Substrate	Patent	Year	Assignee
Specialty	Polybutadiene	W. Germany 2,647,854	1977	Sumitomo Chem.
Latex	Polyisoprene	Japan 999	1977	Kuraray Co.
Specialty	1,2-Polybutadiene	Japan 11,291	1977	Matsushita Electric
General purpose	Ethylene-co-vinyl acetate polymer	Japan 24,387	1978	Toyo Soda
Grafting procedures	Polyolefins	Japan 130,744	1978	Sumitomo Chemical
Tackifiers	Cyclopentadiene resins	W. Germany 2,856,335	1979	Mitsui Petrochemical
PVC adhesives—metal polymer composites	Ethylene-vinyl acetate copolymer, polyethylene	Japan 40	1979	Mitsubishi Chemical
Hot melt	Ethylene-vinyl acetate copolymer	Japan 110,291	1979	Nippon Petrochemicals
Blow molded containers and laminates	Ethylene-propylene copolymer	Japan 113,678	1979	Mitsubishi Chemical
Rubber-metal adhesives	1,2-Polybutadienes	Japan 133,540	1979	Japan Synthetic Rubber
Water-thinned adhesives	Polybutadienes	Japan 134,745	1979	Nippon Oil Co.
Film laminate adhesives	Ethylene-vinyl acetate copolymer	Japan 135,860	1979	Mitsubishi Chemical
Composite molding adhesives	Ethylene-vinyl acetate copolymer	Japan 144,477	1979	Asahi Chemical Ind.
Hot melt	Polyethylene	United States 4,207,220	1980	Eastman Kodak
Polyolefin laminate	Polyethylene	Britain 1,566,495	1980	American Can
Thermoplastic laminates	Tall oil pitch	Canada 1,075,390	1980	Northwood Mills Ltd.
Hot melt	Ethylene-propylene copolymer	Europe 11,474	1980	Mitsui Petrochemical Ind.
Adhesion promotion on brass-coated steel wire	Rubber mix	W. Germany 2,853,462	1980	Continental Gummi-Werke
Adhesives	Vinyl acetate-vinyl fluoride copolymer	W. Germany 2,853,671	1980	Th. Goldschmidt A.G.
Adhesive and coating resins	Polybutadiene	W. Germany 2,948,323	1980	Hitachi Chemical
Plastic film adhesive	Polyethylene	W. Germany 3,012,144	1980	DuPont
Al foil-crystalline polymer laminates	Isotactic polypropylene	Japan 9,804	1980	Toyo Seikan Kaisha, Ltd.
Water-based plywood adhesives	Polybutadienes	Japan 15,510	1980	Nippon Zeon Co.
Polyolefin-polyester laminates	Polyethylene ethylene-propylene copolymer	Japan 62,945	1980	Mitsubishi Chemical

Peelable adhesives	Petroleum resin	Japan 67,452	1980	Japan Crown Cork
Hot melt adhesives	Styrene containing block copolymers	Japan 80,408	1980	Kureha Chemical Ind.
High strength adhesives	Polybutadiene	Japan 28,258	1981	Sekisui Chemical

COATINGS

General purpose	Terpene polymers	United States 2,321,750	1943	Hercules
Tough, flexible	Ethylene-vinyl chloride copolymer	United States 2,497,291	1950	Dupont
Alkyd modifier	Cyclopentadiene polymers	United States 2,608,550	1952	Interchemical
Drying oils	Styrene-butadiene copolymers	United States 2,652,342	1953	Standard Oil
Can	Polybutadienes	United States 2,876,207	1959	DuPont
New resins	$\alpha$ -Methylstyrene-diene copolymers	United States 2,993,057	1961	Esso Research
General purpose	Styrene-co-butadiene	United States 3,025,258	1962	Devoe & Reynolds
Acylated materials	Polystyrene	United States 3,222,323	1962	Dow Chemical
Can	Styrene-co-maleic anhydride	United States 3,097,957	1963	Esso Research
Maleinated resins	Styrene-co-butadiene	W. Germany 1,150,480	1963	Esso Research
General purpose	Polystyrene	United States 3,214,416	1965	Dow Chemical
Adhesion promoters	Polypropylene	Belgium 659,184	1965	Hercules
Resin intermediates	Petroleum resins	France 1,396,452	1965	Esso Standard
Heat curable	Petroleum resins	France 1,401,185	1965	Esso Standard
Metal container	Hydrogenated cyclopentadiene resins	United States 3,240,762	1966	Velsicol Chemical
General purpose	Polyether acetate	Belgium 673,274	1966	Cassella Farbwerke
Polyolefin primers	Polypropylene	France 1,429,618	1966	Hercules
Water soluble	Petroleum waxes	Japan 10,995	1966	Toa Neuryo Kogyo
Granular materials	Polypropylene	Netherlands 3,889	1966	National Cash Register
Photoreactive	Styrene-co-butadiene	U.S.S.R. 178,983(4)	1966	—
Metal	Isotactic 1,3-butadiene-mesityl oxide copolymer	United States 3,351,671	1967	Ford Motor
Polyester and epoxy resin hardeners	Poly(vinyl alkyl ether)	Britain 1,059,255	1967	Cassella Farbwerke
General purpose	Atactic polypropylene	Czechoslovakia 123,974	1967	—
Metal	Hydrogenated poly(butadiene)	France 1,484,302	1967	Esso Research
Rapid drying alkyd	1,4-Polybutadienes	Netherlands 11,754	1967	Chemische Werke Huels



Table A.7 (cont.)

Applications	Substrate	Patent	Year	Assignee
Metal	Polybutadiene	United States 3,365,411	1968	Esso Research
Metal primers	Polypropylene	United States 3,375,300	1968	Hercules
General purpose	Polyolefins	United States 3,399,071	1968	Union Carbide
Electrodeposition	Polybutadiene	Britain 1,102,652	1968	Esso Research
Textile	Polypropylene and propylene-co-1-butene	France 1,516,084	1968	Eastman Kodak
Polyester crosslinker	Polypropylene	Japan 6,795	1968	Chisso Corp.
Masonry	Polyisobutene	United States 3,438,804	1969	Shell Oil
Floor, textiles	Polypropylene	United States 3,480,580	1969	Eastman Kodak
Emulsions for textiles	Polyethylene	Britain 1,141,943	1969	Eastman Kodak
Floor polishes	Polyethylene or polypropylene	France 1,581,572	1969	Eastman Kodak
Photographic films	Polyethylene	W. Germany 1,815,869	1969	Eastman Kodak
Milk Carton	Polyethylene and poly(ethylene-co-vinyl acetate)	W. Germany 1,902,828	1969	U.S. Plywood
Waterborne	1,2- and 1,4-Polybutadienes	United States 3,518,213	1970	Japan Oil
Water soluble	Polyallene	United States 3,541,058	1970	Dow Chemical
Inks and floor polishes	Hydrocarbon waxes	Britain 1,182,161	1970	Petrolite Corp.
Flexible, waterborne	Polybutadiene and poly(styrene-co-butadiene)	France 2,033,758	1970	Japan Soda
Hard, flexible metal	1,2-Polybutadiene	W. Germany 1,813,568	1970	Japan Soda
Oil-alkyd modifier	<i>cis</i> -1,4-Polybutadiene (>80%)	W. Germany 1,815,014	1970	Chemische Werke
General purpose	Polybutadiene (>80% <i>cis</i> -1,4)	W. Germany 1,929,593	1970	Vianova Kunsthaz
General purpose	Hydrocarbon waxes	W. Germany 1,946,357	1970	Dunlop Co.
Water-soluble electrophoretic	Polybutadiene	W. Germany 1,965,669	1970	Vianova Kunsthaz
Styrene-co-maleic polyolefins anhydride grafted	Polyolefins and poly(ethylene-co-vinyl acetate)	W. Germany 2,023,154	1970	Mitsui Polychemical
Specialty	Petroleum resins	Japan 6,823	1970	Japan Oil
Glossy paper	Petroleum resins	Japan 31,684(5)	1970	Hamano Dye Works
Epoxy resin hardener	Polybutadiene	Japan 39,182	1970	Japan Soda
Allyl derivatives for polyesters	Polybutadiene and polyisoprene	U.S.S.R. 276,415	1970	Moscow Technical Inst.

Waterborne	1,4-Polybutadiene	Britain 1,234,230	1971	Japan Soda
Clay particles	Low-density polyethylene	Britain 1,255,310	1971	Champion Paper Co.
Epoxy resin hardener	Polybutadiene	W. Germany 2,013,096	1971	Chemische Werke
Waterborne	1,2-Polybutadiene and SBR	Japan 954	1971	Japan Soda
Water soluble	1,2-Polybutadiene	Japan 7,269	1971	Japan Oils
General purpose	Ethylene-co-vinyl acetate	Romania 52,457	1971	Romania Petrochemic
Metallic binder	Ethylene-co-vinyl acetate polymer	Romania 52,798	1971	Combinatul Petrochimic
Electrophoretic	Polybutadiene	W. Germany 2,116,975	1972	Farbenfabriken Bayer
Waterborne	Polybutadiene	W. Germany 2,120,962	1972	Vianova Kunstharz
Electrophoretic	1,2-Polybutadiene	W. Germany 2,138,447	1972	Kansai Paint Co.
Thermosetting	1,2-Polybutadiene	W. Germany 2,157,886	1972	Matsushita Electric
Electrophoretic	Polybutadienes	W. Germany 2,221,649	1972	Atlantic Richfield
General purpose	Epichlorohydrin-ethylene oxide copolymer	France 2,146,995	1973	Hercules
Abrasion resistant	Dicyclopentadiene-co-ethylene-co-propylene polymer	W. Germany 2,166,358	1973	SNAM Progetti S.p.A.
Electrophoretic	1,2 + 1,4-Polybutadiene	W. Germany 2,237,830	1973	Kansai Paint Co.
Textile antisoiling	Polyethylene and ethylene-co-propylene polymer	W. Germany 2,241,057	1973	Mitsui Petrochemical Ind.
Electrophoretic	Polybutadiene	W. Germany 2,249,432	1973	Vianova Kunstharz
Waterborne	Isoprene rubber	W. Germany 2,305,912	1973	Shell
Electrostatic	Polypropylene	W. Germany 2,326,589	1973	Eastman Kodak
Specialty	Polyolefins	Japan 23,357	1973	Furukawa Electric
Specialty	Polyolefins	Japan 38,790	1973	Toray Industries, Inc.
Electrophoretic	Polybutadiene or SBR (>50%, 1,2)	Japan 42,939	1973	Nippon Soda
Waterproofing	Ethylene-propylene rubber	Japan 42,955	1973	Hirono Chemical
Photoreactive	Polybutadiene	Japan 66,186	1973	Japan Atomic Energy
Latex paint dispersants	Polybutadiene	Japan 73,488	1973	Kansai Paint Co.
Electrophoretic	1,2 and 1,4-polybutadiene	Japan 93,631	1973	Kansai Paint
Corrosion-resistant metal	cis-1,4-Polybutadiene	Japan 95,423	1973	Shinto Paint Co.
Specialty	1,2-Polybutadiene	W. Germany 2,362,534	1974	Nippon Oil
Specialty	Petroleum resins	W. Germany 2,364,169	1974	Societa Italiana
Electrophoretic	Cationic butadiene-co-1,3-pentadiene polymer	W. Germany 2,407,300	1974	Nippon Zeon

Table A.7 (cont.)

Applications	Substrate	Patent	Year	Assignee
Water soluble	Poly(cyclopentadiene)	W. Germany 2,409,130	1974	—
Aqueous, electrocoatings	Polybutadiene	W. Germany 2,411,348(50)	1974	Reichhold-Albert-Chemie
Electrocoatings	Polypentene	W. Germany 2,412,853	1974	Shell
Water soluble	Polybutadiene	Japan 4,059	1974	Dai Nippon Toryo Co.
Electrophoretic	Polybutadiene	Japan 4,292	1974	Dai Nippon Toryo Co.
Rubber paint resins	Butadiene-co-styrene polymer	Japan 13,612	1974	Honny Chemicals
Electrodeposition	Polybutadiene (91% 1,2 and 9% 1,4)	Japan 20,737	1974	Dai Nippon
General purpose	1,3-Polypentadiene	Japan 28,694	1974	Japan Zeon
Epoxy resin hardener	Butadiene-co-isobutylene polymer	Japan 48,798	1974	Mitsubishi Petrochemical
Electrodeposition	1,2- and 1,4-Polybutadienes	Japan 99,134	1974	Nippon Paint
Epoxy resin hardener	Liquid polybutadiene (>60% <i>cis</i> 1,4)	Japan 100,122	1974	Nippon Zeon
Electrophoretic	Butadiene-co-1,3 pentadiene	Japan 108,134	1974	Nippon Zeon
Floor polish	Polybutadienes	Japan 109,489	1974	Toa Gosei Chemical
Specialty	Poly(ethylene-co-butadiene)	Japan 122,591	1974	Mitsui Petrochemical
Alt. styrene-co-maleic anhydride grafted polyolefins	Polyolefin waxes	United States 3,883,458	1975	BASF A.G.
Electrophoretic	Polybutadiene (>60% <i>cis</i> ), poly(1,3-pentadiene) <i>trans</i> >70%)	United States 3,897,260	1975	Nippon Zeon
Waterborne	Blends liquid 1,3-butadiene and 1,3-pentadiene polymers	United States 3,920,769	1975	Nippon Zeon
Electrophoretic	1,3-Polypentadiene	W. Germany 2,259,120	1975	—
Specialty	Polybutadiene (>78% <i>cis</i> -1,4)	W. Germany 2,349,625	1975	Reichhold-Albert-Chemie
Specialty	Diolefin polymers	W. Germany 2,357,762	1975	Hoechst A.G.
Electrophoretic	Polybutadienes	W. Germany 2,411,349	1975	Hoechst A.G.
Water-thinnable electrocoatings	Polybutadiene	W. Germany 2,411,419	1975	Hoechst A.G.
Thermoplastics	Polybutadienes	W. Germany 2,427,847	1975	Nippon Oil
Electrophoretic	Butadiene-co-1,3-pentadiene	W. Germany 2,446,891	1975	Nippon Zeon



Water soluble	Polyalkyl dienes	W. Germany 2,449,271	1975	Vianova Kunstharz A.G.
Water soluble	Polybutadiene	W. Germany 2,452,432	1975	Nippon Oil
Powder	Polypropylene	W. Germany 2,454,808	1975	Eastman Kodak
Water soluble—electrodeposition	Polybutadiene (70% <i>cis</i> -1,4; 28% 1,4- <i>trans</i> )	W. Germany 2,507,809	1975	Vianova Kunstharz A.G.
Electrodeposition	Polybutadiene	W. Germany 2,510,579	1975	Imperial Chem.
Epoxy curing agent	Polybutadiene	W. Germany 2,513,123	1975	French Petroleum Institute
Electrodeposition	Polybutadiene	Japan 1,582	1975	Dai Nippon Toryo Co.
Electrophoretic	Polybutadiene (>89% 1,2)	Japan 18,588	1975	Nippon Oils and Fats
Maleic anhydride-co-acrylic acid grafted coatings for polyolefin fillers	Poly(ethylene-co-vinyl acetate)	Japan 27,842	1975	Toyo Soda Mfg. Company
Epoxy resin hardener	1,3-Polypentadiene	Japan 30,997(8)	1975	Asahi Electrochemical
Pigment	Isoprene oligomers	Japan 58,122	1975	Mitsubishi Petrochemical
Water-soluble resins	Butadiene, isoprene and chloro-prene polymers	Japan 71,794	1975	Pentel Paint Co.
Electrophoretic resins	Liquid polybutadiene (83% 1,2 and 17% <i>trans</i> 1,4-)	Japan 87,490	1975	Japan Oil
Antistatic	Polystyrene and Poly(vinyl chloride)	Japan 115,277	1975	Sekosha KK
Waterborne	Polybutadiene (thermal)	Japan 126,724	1975	Kansai Paint
Traffic marker	Liquid 1,3-polypentadiene	Japan 130,827	1975	Nippon Zeon
Traffic marker	Hydrocarbon resins	Japan 142,630	1975	Nippon Zeon
Water soluble	Diene polymers	Japan 144,796	1975	Pentel Co.
Electrophoretic	Polybutadiene	Japan 149,730	1975	Nippon Paint
Air dry and printing inks	Liquid <i>cis</i> -1,4-polybutadiene	W. Germany 2,604,680	1976	Sumitomo Chem.
Electrophoretic	Polyisoprene	United States 4,024,095	1977	Hoechst A.G.
Light curable	Poly(butadiene)	United States 4,038,084	1977	UBE Industries
Water dilutable electrophoretic	Polybutadiene	Belgium 848,777	1977	Herberts K. Co.
Rapid air dry	Polybutadiene	Britain 1,486,711	1977	Kansai Paint
Specialty	High mol. wt. 1,2-polybutadiene	Britain 1,493,185	1977	Japan Synthetic
Specialty	Polybutadiene	W. Germany 2,647,854	1977	Sumitomo Chem.
Floor polishes and inks resins	Polyolefin waxes	W. Germany 2,710,025	1977	Nippon Oil
Specialty	1,2-Polybutadiene	Japan 11,291	1977	Matsushita Electric
Waterborne	1,3-Polypentadiene	Japan 33,981	1977	Seiko Chemical

Table A.7 (cont.)

Applications	Substrate	Patent	Year	Assignee
Dispersants for emulsion paints	Polyalkenes	Japan 33,982	1977	Nippon Paint Co.
Waterborne	1,2-Polybutadiene	Japan 35,224(6)	1977	Kansai Paint
Anticorrosive	Polybutadiene	Japan 42,529	1977	Kansai Paint
Specialty	Polybutadiene	Japan 42,538	1977	Ohtsu Tire and Rubber
Allyl alcohol derivative-photocurable coatings	Rubbers	Japan 81,396	1977	Showa Highpolymer
Composites	Polyethylene, polypropylene, and terpolymers	Japan 93,495(6,7)	1977	Mitsubishi Chem.
Corrosion-resistant, electrodeposition	Polybutadiene	Netherlands 13,983	1977	Herberts K. Co.
Aqueous dispersions	Polybutadienes	Japan 5,232	1978	Kansai Paint
Latex dispersin	Polybutadienes	Japan 8,630	1978	Kansai Paint
Acrylic derivatives, photocurable resins	Polybutadiene	Japan 28,351	1978	UBE Industries
Steel pipe linings	Polyolefins with anthracene	Japan 61,679	1978	Mitsubishi Chemical
Electrophoretic	Polybutadienes	Japan 142,444	1978	Nippon Oil
Specialty	Diene polymers and copolymers	United States 4,161,571	1979	Sumitomo Chemical
Electrocoatings	Diene polymers	United States 4,176,110	1979	Nippon Oil Co.
Waterborne	Poly(1,4- <i>cis</i> -butadiene)	Austria 350,157	1979	Herberts G.m.b.H.
Aqueous coating compositions	Polybutadienes	Austria 352,843	1979	Vianova Kunsthartz
Water dilutable imide coatings	Poly(1,4- <i>cis</i> -butadiene)	Britain 1,533,861	1979	Dr. Kurt Herberts & Co.
Anionic film forming binder	Polybutadiene	Britain 2,737,755	1979	BASF A.G.
Crosslinkable resins	Butadiene-styrene rubber	France 2,402,675	1979	Elastomer, Rubber Mfg.
Floor polishes	Ethylene-propylene copolymer	W. Germany 2,852,743	1979	Nippon Oil
Powder coating compositions	Polyethylene	W. Germany 2,914,270	1979	Mitsui Petrochemical
Epoxy resin curing agents	Petroleum fractions	W. Germany 3,006,704	1979	Nippon Oil Co.
Hot melt traffic paints	Petroleum resins	Japan 3,845	1979	Sumitomo Chemical
Waterborne	Polybutadiene	Japan 6,025	1979	Japan Geon
Anticorrosive	Conjugated diene polymers	Japan 8,132	1979	Ashai Chemical
Abrasion-resistant coatings	Ethylene-propylene-norbornene copolymer	Japan 17,931	1979	—

Rapid drying emulsion coatings	Polybutadiene	Japan 25,530	1979	Kansai Paint
Metal coatings	Polyethylene	Japan 43,992	1979	Nippon Petrochemical
Electrophoretic	Diene polymers	Japan 71,123	1979	Nippon Oil Co.
Latex emulsifions	Polybutadiene	Japan 87,738	1979	Kansai Paint Co.
Hot-melt traffic paint	Polyethylene	Japan 106,542	1979	Mitsui Petrochemical Ind.
Photocurable compositions	Diene polymers	Japan 129,044	1979	UBE Industries
Hot-melt traffic marking paints	Petroleum resins	Japan 133,524	1979	Sumitomo Chemical Co.
Water-thinned coatings	Polybutadiene	Japan 143,444	1979	Vianova Kunstharz A.G.
Block copolymer latexes	Styrene-butadiene block copolymer	Japan 146,831	1979	Kuraray Co.
Block copolymer latexes	Styrene-butadiene copolymers	Japan 148,889	1979	Kuraray Co.
Electrodeposition resins	1,2-Polybutadiene	Japan 157,135	1979	Dainippon Toryo Co.
Light-curable compositions	Polybutadiene	Japan 160,491	1979	UBE Industries
Synthetic drying oils	Low mol. wt. polydienes	U.S.S.R. 679,608	1979	Chuvash State University
Corrosion-resistant electrodeposition coatings	Polybutadiene resins	United States 4,209,598	1980	Herberts K. Co.
Electrodeposition coatings	<i>cis</i> -1,4-polybutadiene	Australia 355,155	1980	Herberts G.m.b.H.
Electrophoretic compositions	1,2-Polybutadiene	Britain 1,563,682	1980	Nippon Oil Co.
General purpose	Polydienes	Britain 1,579,338	1980	Int. Paint Co.
General purpose	Polybutadienes	Britain 2,048,941	1980	Polymer Investments
Polymer-coated siliceous fillers	Polybutadiene	Europe 7,190	1980	Imperial Chemical
Chlorinated copolymer for coatings	Poly- $\alpha$ -olefins	W. Germany 2,005,482	1980	Eastman Kodak
Photocurable resins	Polybutadiene	W. Germany 2,614,860	1980	IBE Ind.
Water-thinnable resins	Polybutadiene	W. Germany 2,828,727	1980	BASF A.G.
Cathodic electrodeposition	Diene polymers	W. Germany 2,934,172	1980	Kansai Paint Co.
Drying oils	Polydienes	W. Germany 2,941,595	1980	French Petroleum Institute
Electrolytic compositions	Polybutadiene	W. Germany 2,944,082	1980	Nippon Oil Co.
Glass fiber sizes	Polypropylene	W. Germany 3,003,251	1980	PPG Ind.
Electrophoretic materials	Polybutadienes	Japan 5,932	1980	Kansai Paint Co.
Steel pipe coatings	Poly(1,3-pentadiene)	Japan 5,935	1980	Nippon Paint Co.
Electrophoretic coatings	Polybutadiene	Japan 17,116	1980	Nippon Oils and Fats
Water-based paints	Diene polymers	Japan 43,150	1980	Sekisui Chemicals Ind.
Electrophoretic	Polydienes	Japan 69,669	1980	Sumitomo Chemical



Table A.7 (cont.)

Applications	Substrate	Patent	Year	Assignee
Crosslinked film materials	Polyisoprene	Japan 84,335	1980	Kuraray Co.
Coating materials	1,2-Polybutadiene	Japan 94,905	1980	Nippon Oil Co.
Waterborne coating	Polybutadiene	Japan 120,604	1980	Nippon Oil
Specialty	Polybutadiene	Japan 139,465	1980	Mitsubishi Heavy Ind.
Water-dilutable electrophoretic coatings	Polybutadiene	Europe 6,563	1981	BASF A.G.
CONTROLLED RELEASE POLYMERS				
Pest control carrier	Polyethylene wax	United States 3,281,319	1966	Union Carbide
ELASTOMERS				
Improved vulcanizates	Natural rubber	France 972,455	1951	—
Modified rubbers	Diene polymers	United States 2,662,874	1953	B. F. Goodrich
Elastomers and textile adhesives	Rubber	United States 2,844,502	1958	U.S. Rubber
Improved rubber vulcanizates	Butyl rubber	United States 2,845,403	1958	U.S. Rubber
Modified vulcanizates	Isoprene, butadiene, and butene-1 copolymers	Italy 574,913	1958	Montecatini
Modified vulcanizates	Olefin-diene copolymers	W. Germany 1,050,059	1959	Esso Research
Saturated	Ethylene-co-propylene	Britain 855,969	1962	Montecatini
Saturated	Ethylene-co-propylene	Belgium 620,705	1963	Montecatini
Rubbers with reduced cold flow	cis 1,4-Polybutadiene (>85% cis)	Britain 952,021	1964	Phillips Petroleum
Vulcanized rubber modifier	Halogenated butyl rubber	United States 3,255,154	1966	Esso Research
Rubbers with reduced cold flow	Rubber (thermal)	Britain 1,018,364	1966	Phillips Petroleum
Vulcanization modifier	Styrene-butadiene rubber	France 1,436,602	1966	Farbenfabriken Bayer
Modified rubbers	Ethylene-propylene-diene (EPDM) rubber	Netherlands 3,457	1966	U.S. Rubber
Improved rubbers	Polybutadiene, SBR and butadiene-co-isoprene rubbers	France 1,506,155	1967	Asahi Chemical

Rubbers with improved green strength	<i>cis</i> -1,4-Polyisoprene	Netherlands 7,078	1967	Shell
Vulcanizable	Ethylene-propylenedicyclopentadiene terpolymer	France 1,551,717	1968	Chemische Werke Huels
Improved tensile strength	Diene rubbers (thermal)	South Africa 1,297	1968	Shell
Rubber crosslinker	Ethylene-co-propylene	Britain 1,148,855	1969	Farbwerke Hoechst
Thermoplastic rubbers	Polyisoprene	Britain 1,158,980	1969	Shell
Vulcanizable rubbers	Polyisoprene	Britain 1,168,388	1969	Shell
Rubber composites with improved impact	Polybutadiene and polyisoprene	W. Germany 1,301,508	1969	Chemische Werke Huels
Modified rubbers for improved strength	Polybutadienes	W. Germany 1,816,723	1969	Shell
Rubbers with improved green strength	Lithium prepared poly(isoprene)	United States 3,527,736	1970	Shell Oil
Modified rubbers	Diene-olefin copolymers	Japan 21,732	1971	Toyo Soda
Ionic crosslinked butyl rubber	Chlorinated butyl rubber	United States 3,646,166	1972	Esso Research
Rubbers with improved tensil and modulus	Isoprene rubber	W. Germany 2,143,804	1972	SNAM Progetti S.p.A.
Abrasion resistant	Dicyclopentadiene-co-ethylene-co-propylene polymer	W. Germany 2,166,358	1973	SNAM Progetti S.p.A.
Nonsulfur vulcanizable	Ethylene (55%)-propylene (40%)-dehydroisodicyclopentadiene (5%) polymer	United States 3,803,092	1974	SNAM Progetti S.p.A.
Rubbers with improved green strength	<i>cis</i> -1,4-Polyisoprene	W. Germany 2,342,434	1974	Kuraray Co.
Rubbers with improved green strength	Isoprene rubber	W. Germany 2,357,149	1974	Kuraray Co.
Improved rubbers	Polyisoprene	W. Germany 2,357,368(9)	1974	Kuraray Co.
Thermoplastic elastomers	Ethylene-co-diene copolymers	W. Germany 2,401,149	1974	DuPont
Specialty	Ethylene-co-propylene	Japan 55,794	1974	Mitsui Petrochemical
Improved rubbers	<i>cis</i> -1,4-Polyisoprene	Japan 71,027	1974	Kuraray Co.
Improved rubbers	<i>cis</i> -1,4-Polyisoprene	Japan 78,739	1974	Kuraray Co.
Improved tire tread rubbers	<i>cis</i> -1,4-Polyisoprene	Japan 86,464	1974	Kuraray Co.
Rubbers with improved green strength	<i>cis</i> -1,4-Polyisoprene	Japan 121,892	1974	Kuraray Co.

Table A.7 (cont.)

Applications	Substrate	Patent	Year	Assignee
Rubbers with improved tack	$\alpha$ -Olefin-co-piperylene polymer	United States 3,929,737	1975	Goodyear Tire
Allyl derivatives in improved rubbers	Butadiene homo and copolymers	Japan 66,591	1975	Toa Gosei Chemical
Rubbers with improved green strength	<i>cis</i> -1,4-Polyisoprene	Japan 67,390	1975	Kuraray Co.
Improved rubbers	1,2-Polybutadiene	Japan 117,889	1975	Japan Synthetic Rubber
Aqueous rubber dispersions	<i>cis</i> -1,4-Polyisoprene	Japan 127,950	1975	Kuraray Co.
Easily curable coating resins	Low mol. wt. poly(butadiene)	United States 3,974,129	1976	Shell
Moisture curable	Isoprene-co-isobutene polymers	United States 4,048,258	1977	Exxon Research
Rubbers with improved properties	<i>cis</i> -1,4-Polyisoprene (>80% <i>cis</i> -1,4)	W. Germany 1,745,387	1977	Shell
Rubbers with improved modulus and tensile strength	Thermoplastic polyolefin elastomers	W. Germany 2,646,480	1977	Mitsui Petrochemical
Rubbers vulcanizable with weak acid metal salts	Ethylene terpolymer with propylene and 1,4-hexadiene	Japan 43,677	1977	DuPont
Rubber tackifier	Piperylene-co- $\alpha$ -olefin polymers	Britain 1,503,160	1978	Goodyear Tire & Rubber
Metal oxide modified and moisture-cured elastomers	Butyl rubber with conjugated olefin residues	Britain 1,522,628	1978	Exxon Research
Thermoplastic elastomers	Ethylene-propylene-1,4-hexadiene terpolymer	Japan 19,351	1978	DuPont
Thermoplastic elastomers	Conjugated diene polymers	Netherlands 157,316	1978	Shell
Impact-resistant copolymers	SBR	United States 4,172,861	1979	Standard Oil
New rubber vulcanizates	Chloroprene rubber	U.S.S.R. 649,997	1979	Siberian Technical Inst.
Improved vulcanizable rubbers	Petroleum resins	U.S.S.R. 673,647	1979	—
Improved rubber compositions	Liquid isoprene rubber	W. Germany 2,854,892	1980	Kuraray Co.
Sealing compositions	Li prepared polyisoprene	W. Germany 2,935,846	1980	Kuraray Co.
Abrasion-resistant rubber	Polybutadiene	Japan 20,482	1980	Bridgeston Tire
Water-resistant elastomers	Ethylene- $\alpha$ -olefin copolymers	Japan 23,842	1980	Mitsui
Elastomers	Polyisoprenes	Japan 41,257(258)	1980	Kuraray
Elastomers	Polyisoprenes	Japan 41,613	1980	Kuraray
Rubber vulcanizates with improved mooney	Isoprene rubbers	Japan 48,231	1980	Kuraray



Rubber–fabric laminates	Polyisoprene	Japan 84,656(7)	1980	Kuraray
Improved vulcanizates	Isoprene rubbers	Japan 106,247	1980	Kuraray
Elastomers, additives	Polyisoprene	Japan 133,403	1980	Kuraray
Elastomers	Polyisoprene	Japan 135,106	1980	Kuraray
Thermoplastic elastomers	Ethylene–propylene copolymer	W. Germany 2,646,480	1981	Mitsui Petrochemical

EMULSIFIERS AND DISPERSANTS

Emulsifying agents	Styrene–isobutylene copolymer	United States 2,871,137	1958	Esso Research
Latex coating pigments	Ethylene–propylene copolymers	United States 3,255,130	1966	Hercules
Aqueous metal working lubricants	Polyolefins, polyisoprene poly(styrene butadiene)	France 1,505,020	1967	Union Carbide
Emulsion stabilizers	$\alpha$ -Olefin polymers	Britain 1,154,433	1969	Eastman Kodak
Latex	Hydrocarbon resins	United States 3,655,629	1972	M. Takahara
Vinyl polymer	Polybutadienes and butadiene copolymers	W. Germany 2,216,175	1972	Kansai Paint
Paint pigment dispersants	Propylene, propylene–co–ethylene, 1-butene, styrene, and 1,2-poly-butadiene polymers	Japan 47,594	1972	Nippon Oils and Fats
Vinyl polymer dispersant	Polybutadiene (thermal)	Japan 66,784	1974	Kansai Paint Co.
Polymer dispersing agent	Polyisobutylene	Belgium 845,286	1977	Shell
Dispersants for vinyl polymerization	1,2-Polybutadiene, styrene, $\alpha$ -methyl–styrene, and vinyl toluene–butadiene copolymers	Japan 33,937	1977	Kansai Paint
Emulsifiers for polymer dispersions	Polybutadienes	Japan 35,238	1977	Kansai Paint
Dispersants for coating pigments	Polybutadiene	W. Germany 2,910,416	1979	Nippon Oil Co.
Polymeric emulsifiers	Isoprene resins	Japan 126,289	1979	Sekisui Chemical Co.

FIBERS

Improved nylons	Nylon 66	Britain 838,413	1960	DuPont
Polyolefins with improved dyeability	Polypropylene fiber	Britain 850,471	1960	Montecatini

Table A.7 (cont.)

Applications	Substrate	Patent	Year	Assignee
Nylons with improved moisture absorption	Nylons	Belgium 623,166	1963	Yardney Int.
Improved dyeability and moisture regain	Polypropylene	Czechoslovakia 106,405	1963	—
Improved dyeability	Polypropylene	United States 3,131,990	1964	Montecatini
Polyolefins with improved dyeability	Olefin-co-diolefin, olefin-co-acetylene polymers	Belgium 655,390	1965	Badische Anilin
Nylons with improved wettability	Nylon	United States 3,297,786	1967	Yardney Int.
Glass sizing agents	Polybutadiene	United States 3,414,432	1968	Esso Research
Polyolefins with improved dyeability	Polypropylene	Japan 3,974	1968	Chisso Corp.
Fabric coatings	Polyethylene wax	United States 3,450,559	1969	Union Carbide
Chorinated fire-retardant fabrics	Poly(ethylene-co-propylene)	United States 1,581,819	1969	Farbwerke Hoechst
Improved dyeability	Polyester	France 2,004,244	1969	Japan Atomic
Dyeable polyolefins	Polypropylene	Japan 1,540	1969	Mitsubishi Rayon
Improved dyeability	Polypropylene	Japan 19,863	1969	Mitsubishi Rayon Co.
Nylons with enhanced dyeability	Nylon fabric	United States 3,488,268	1970	DuPont
Hydrophilic polypropylene	Polypropylene	Japan 3,838	1971	Mitsubishi Rayon
Improved dyeability	Polypropylene	Japan 27,579	1971	Mitsubishi Rayon
Polyolefin-nylon blends	Polypropylene, polystyrene	Japan 38,836	1971	Mitsubishi Rayon
Improved dyeability	Nylon	United States 3,670,048	1972	DuPont
Textile antisoiling	Polyethylene and ethylene-co-propylene polymer	W. Germany 2,241,057	1973	Mitsui Petrochemical Ind.
Antistatic and hydrophilic textiles	Nylon	Japan 39,795	1973	Toray Industries, Inc.
Polyolefins with dyeability improvement	Polypropylene	Japan 44,186	1978	Mitsui Petrochemical Ind.
Polyolefins with improved dyeability	Polypropylene	W. Germany 2,708,757	1979	Idemitsu Ind.

FILMS

Thermoplastic, water impermeable	Poly(vinylidene chloride)	Belgium 525,249	1954	Sidac
Modified cellophanes	Natural rubber	Japan 7,493	1954	Dai Nippon Cellophane
Extradable	Polyethylene	Belgium 616,255	1962	Union Carbide
Extradable thermoplastics	Petroleum waxes	Netherlands 6,219	1964	Societe Nationale
Polyolefin	Polyolefins	Netherlands 6,926	1965	Kalle A.G.
Polyolefins with improved surface properties	Polypropylene	United States 3,286,009	1966	Toyo Rayon
Polyolefins with improved dyeability	Polyethylene	United States 3,290,415	1966	DuPont
Modified polyolefins	Polypropylene	U.S.S.R. 192,329	1967	All-Union Scientific Research Institute
Packaging	Polyethylene	France 1,514,019	1968	Eastman Kodak
Polyolefins with improved dyeability	Polypropylene	Japan 3,974	1968	Chisso Corp.
Improved dyeability	Polypropylene	Japan 27,421(2)	1968	Mitsubishi Rayon
Improved dyeability	Polyacrylonitrile	U.S.S.R. 218,373	1968	—
Polyolefin-aluminum laminates	Hydrocarbon polymers	United States 3,450,560	1969	Chevron Research
General purpose	Polystyrene	W. Germany 1,298,710	1969	Badische Anilin
Photographic	Polyethylene	W. Germany 1,815,869	1969	Eastman Kodak
Crosslinked polyolefins	Polyethylene	U.S.S.R. 223,306	1969	All-Union Scientific Research Institute
Laminated	Polyolefins	United States 3,503,786	1970	Eastman Kodak
Polypropylene with improved adhesion	Polypropylene	United States 3,579,486	1971	Eastman Kodak
Hydrophilic polypropylene	Polypropylene	Japan 3,838	1971	Mitsubishi Rayon
Improved dyeability	Polypropylene	Japan 27,579	1971	Mitsubishi Rayon
Enhanced strength	Polystyrene	United States 3,661,866	1972	Kimberly-Clark
Blow molded multilayer plastic bottles	Polyolefins	France 2,132,395	1972	Mitsui Petrochemical
Acrylic ester-co-maleic anhydride grafted	Ethylene-co-vinyl acetate polymer	W. Germany 2,147,318	1973	Toyo Soda
Ethylene-propylene-diene rubber	Polybutadiene	W. Germany 2,326,198	1973	Revertex Ltd.
High tenacity	Polycyclopentadiene	Japan 42,231	1973	Nippon Zeon
Photographic	Gelatin	United States 3,837,861	1974	DuPont



Table A.7 (cont.)

Applications	Substrate	Patent	Year	Assignee
Moldings	Polyethers	Britain 1,358,184	1974	Hercules
<i>endo</i> -Bicyclo[2.2.1] carboxylic anhydride graft—dye assist grafting	Polypropylene	W. Germany 2,524,866	1976	Toa Nenryo
Improved PVC materials	Poly(vinyl chloride)	Japan 5,939	1977	Japan Catalytic
PVA Blends	Polyolefin	Japan 62,362	1977	Nippon Petrochemical
Composites	Polyethylene, polypropylene, and terpolymers	Japan 93,495(6,7)	1977	Mitsubishi Chem.
Blood compatible thermoplastics	Polyolefins	Belgium 868,208	1978	Hoechst A.G.
Acrylic derivatives, photocurable resins	Polybutadiene	Japan 28,351	1978	UBE Industries
Polyolefins with dyeability improvement	Polypropylene	Japan 44,186	1978	Mitsui Petrochemical Ind.
Steel pipe linings	Polyolefins with anthracene	Japan 61,679	1978	Mitsubishi Chemical
Anionic film forming binder	Polybutadiene	Britain 2,737,755	1979	BASF A.G.
Nongelling film formers	Butadiene polymers	W. Germany 2,362,534	1979	Nippon Oil Co.
Packaging laminates	Ethylene–vinyl acetate copolymer	Japan 57,582	1979	Asahi–Dow Ltd.
Electret films	Polypropylene	Japan 108,299	1979	Mitsui Petrochemical Ind.
Laminates	Ethylene–vinyl acetate copolymer	Japan 110,282	1979	Nippon Petrochemical
Polypropylene with improved dye receptivity	Polypropylene	Japan 124,095	1979	Idemitsu Kosan Co.
Liquid crystalline compositions	Poly(4-methyl-1-pentene)	Japan 149,386	1979	Mitsui Petrochemical Ind.
Laminated plastic films	Polypropylene	Japan 160,481	1979	Mitsui Petrochemical Ind.
Packaging laminates	Ethylene–propylene block copolymer	Japan 25,325	1980	Toyo Seikan Kaisha, Ltd.
Multilayer containers	Polypropylene	Japan 71,241	1980	Toppan Printing Co.
CELLULAR MATERIALS				
Artificial sponges	Polyethers	France 1,348,550	1964	Pneumatiques
Crosslinked sheets	Poly(vinyl chloride)	United States 3,200,089	1965	Kleber Colombes

Styrene-co-maleic anhydride grafted cellular products	Polypropylene	France 1,411,704	1965	Pneumatiques
Cellular polyolefins	Polyethylene	Japan 47,565	1973	Toray Industries, Inc.

GRAFTING PROCEDURES

Grafting procedures	Olefin polymers	United States 2,589,069	1952	Standard Oil
Grafting procedures	$\alpha$ -Methylstyrene copolymer	United States 2,837,496	1958	Hercules
Grafting procedures	Polyolefins (ethylene and propylene)	United States 2,973,344	1961	Esso Research
Grafting procedures	Polyethylene or polypropylene	France 1,322,846	1963	Pneumatiques
Grafting procedures	Petroleum resins	France 1,368,241	1964	Esso Standard
Grafting procedures	Polyethylene	Poland 52,984	1967	Politechnika Warszawska
Grafting procedure	Polyolefins	Poland 53,137	1967	Politechnika Warszawska
Grafting procedures	Polypropylene	United States 3,499,812	1970	Hercules
Grafting procedures	Polyolefins	Japan 30,943(5)	1970	Mitsubishi
Grafting procedures	Allyl chloride oligomers	Japan 29,495	1971	—
Grafting procedures	Low mol. wt. 1,2-polybutadiene	Britain 2,147,639	1972	Kansai Paint
Styrene-co-maleic anhydride grafting procedures	Polyolefins	France 2,103,060	1972	Lubrizol
Grafting procedures adhesives	1,2-Polybutadiene	W. Germany 2,147,639	1972	Kansai Paint
Grafting procedures	Poly(vinyl chloride)	W. Germany 2,359,051	1974	Hooker Chemical
Styrene-co-maleic anhydride grafted	Polyphenylene ether	Japan 12,953	1974	Asahi Dow
Grafting procedures	Polybutadiene (>50% cis-1,4)	Japan 98,493	1974	Toa Gosei Chemical
Grafting procedures	Polybutadiene	Japan 99,695	1974	Toa Gosei Chemical
Grafting procedures	Liquid polybutadiene polyisoprene	Japan 113,893	1974	Sumitomo Chemical
Grafting procedures	Polybutene	United States 3,960,900	1976	Standard Oil
Grafting procedures	Liquid polybutadiene and polyisoprene copolymers	Japan 39,436	1977	Sumitomo Chem.
Grafting procedures	1,2-Polybutadiene SBR isoprene-butadiene copolymer	Japan 58,790	1977	Kansai Paint
Grafting procedure	1,2-Polybutadiene	Japan 78,993	1977	Japan Synthetic
Grafting with imidazoles	Liquid polybutadiene polyisoprene and copolymers	United States 4,080,493	1978	Sumitomo Chem.

Table A.7 (cont.)

Applications	Substrate	Patent	Year	Assignee
Grafting procedures	High mol. wt. 1,2-polybutadiene	United States 4,082,817	1978	Japan Synthetic
Grafting procedures	Synthetic rubbers	Britain 1,529,274	1978	British Petroleum
Production with phenothiazine to prevent gelation	<i>cis</i> -1,4-Polybutadiene	Japan 1,799	1978	Toa Gosei
Maleic acid grafting	Polyolefins	Japan 11,986	1978	Toyo Ink
Grafting procedures	Polyolefins	Japan 130,744	1978	Sumitomo Chemical
Grafting procedures	Polyethylene	United States 4,147,740	1979	General Electric
Grafting procedures	Polyisoprene	Britain 1,538,601	1979	Sumitomo Chemical
Grafting procedures	Diene polymers	Japan 13,478	1979	Sumitomo Chemical
Heterogeneous grafting procedure	Polyethylene, ethylene copolymers	Japan 30,715	1979	Toyo Soda Mfg. Co.
Grafting procedures	Polypropylene	Japan 112,990	1979	Idemitsu Kosan
Grafting procedures	Polypropylene	Japan 12,450	1980	Idemitsu Kosan
Grafting procedures	Isotactic polypropylene	Japan 23,134	1980	Mitsui Toatsu Chemicals
Grafting procedure	Ethylene-vinyl acetate copolymer	Japan 23,571	1980	Toyo Soda Mfg.
Grafting procedures	Polyethylene	Japan 23,572	1980	Toyo Soda Mfg.
Grafting procedures	Polyethylene	Japan 27,336	1980	Nippon Oil Co.
Grafting procedures	Polyolefins	Japan 34,224	1980	Mitsui Toatsu Chemicals
Grafting procedures	Polyethylene	Japan 43,110	1980	Toyo Soda Mfg.
Grafting procedures	Polypropylene	Japan 50,007(8)	1980	Idemitsu Kosan
Grafting procedures	1,4-Polybutadiene polyisoprene SBR, NBR	Japan 75,408	1980	Sekisui Chemicals Ind.
Grafting without gelation	Styrene-diene block copolymers	Japan 98,204	1980	Deni Kagaku Kogyo
Cation grafting	Polystyrene	U.S.S.R. 713,873	1980	—
Improved grafting procedures	Polyisobutylene	United States 4,255,340	1981	Texaco Inc.

ION-EXCHANGE MATERIALS

Modified resins	Styrene-divinyl benzene	United States 3,332,890	1967	Dow Chemical
Modified resins	Poly(vinyl acetate)	U.S.S.R. 214,806	1968	Institute of Textile and Light Ind.



LAMINATES

Polyolefin-metal Moldings	Styrene-diene copolymers	W. Germany 1,109,295	1959	Esso Research
Acylated materials	Polyolefins	France 1,255,075(7)	1960	Polyplastic
Grafted Alt. styrene-maleic anhy- dride	Polystyrene	United States 3,222,323	1962	Dow Chemical
	Chlorinated polyethylene	United States 3,143,521	1964	W. R. Grace
Improved molding resins	Polyethylene	United States 3,177,270	1965	Dow Chemical
General purpose	Polystyrene	United States 3,214,416	1965	Dow Chemical
PVC modifier for moldings	Polybutadiene	Britain 997,318	1965	BTR Industries
Polyolefin moldings	Polyethylene	United States 3,267,083	1966	Union Carbide
Polyolefins with improved surface properties	Polypropylene	United States 3,286,009	1966	Toyo Rayon
Molding resins	Stereoregular polypropylene	Netherlands 7,411	1966	Hercules
Castings with improved adhesion	Stereoregular polypropylene, ethy- lene-propylene copolymers	Netherlands 15,768	1966	Hercules
General purpose	Polyethylene	Poland 51,836	1966	Politechnika Warszawska
Glass reinforced polyolefins	Polypropylene	Britain 1,094,439	1967	Hercules
Reinforced thermoplastics	Polypropylene	Britain 1,095,700	1967	Imperial Chemical
General purpose	Atactic polypropylene	Czechoslovakia 123,974	1967	—
Polyolefin dye assist agents	Hydrocarbon resins	Japan 10,727	1967	Chisso Corp.
Modified polyolefins	Polypropylene	U.S.S.R. 192,329	1967	All-Union Scientific Research Institute
Resin production	Propylene oxide-co-butadiene monoxide polymer	United States 3,398,126	1968	Allied Chemical
General purpose	Polyolefins	United States 3,399,071	1968	Union Carbide
Polyester crosslinker	Polypropylene	Japan 6,795	1968	Chisso Corp.
Improved dyeability	Polypropylene	Japan 27,421(2)	1968	Mitsubishi Rayon
Al-paper laminates	Polypropylene, poly(propylene-co- 1-butene), poly(propylene-co- pentene) and polybutene	United States 3,433,777	1969	Eastman Kodak
High flex strength moldings	Polypropylene	United States 3,437,550	1969	Hercules
General purpose	Polystyrene	W. Germany 1,298,710	1969	Badische Anilin
Moldings	Poly(vinyl chloride)	W. Germany 1,911,465	1969	Firma Karl Egger Kunststoffwerke

Table A.7 (cont.)

Applications	Substrate	Patent	Year	Assignee
Ionic crosslinked moldings	Polypropylene	Japan 15,422(3)	1969	Mitsubishi Rayon Co.
Crosslinked polyolefins	Polyethylene	U.S.S.R. 223,306	1969	All-Union Scientific Research Institute
Styrene-co-maleimic acid poly-olefins anhydride grafted	Poly olefins and poly(ethylene-co-vinyl acetate)	W. Germany 2,023,154	1970	Mitsui Polychemical
Allyl derivative polyesters	Polybutadiene and polyisoprene	U.S.S.R. 276,415	1970	Moscow Technical Institute
Polypropylene with improved adhesion	Polypropylene	United States 3,579,486	1971	Eastman Kodak
Styrene-co-maleic anhydride grafts—impact-resistant thermoplastics	Acrylonitrile polymer	W. Germany 1,949,487	1971	Badische Anilin
Molding resins	Polyolefin	W. Germany 2,061,180	1971	Asahi Chemical
Improved thermoplastic—glass composite	Polyethylene, polystyrene, and poly(4-methyl-1-pentene)	Japan 32,147	1971	Mitsubishi Rayon
Polyolefin-nylon moldings	Polyethylene, polypropylene, and polystyrene	Japan 38,022	1971	Mitsubishi Rayon
Tough, hard compression moldings	Isotactic poly(epichlorohydrin)	United States 3,632,840	1972	Hercules
Decorative polyolefin plastics	Polypropylene	United States 3,697,465	1972	Eastman Kodak
Blow molded multilayer plastic bottles	Polyolefins	France 2,132,395	1972	Mitsui Petrochemical Ind.
Molding materials	Polybutadiene	W. Germany 2,125,957	1972	Hooker Chemical
Styrene-co-maleic anhydride grafted polyolefins	Polypropylene	W. Germany 2,127,841	1972	Mitsui Petrochemical
Reinforced moldings	Polypropylene	France 2,207,940	1974	Imperial Chemical
Polyolefins with improved adhesion	Polypropylene	France 2,208,778	1974	Imperial Chemical
Polyolefin-metal laminates	HD polyethylene	Japan 98,484	1974	Sumitomo Chemical
Polyamide-polyolefin moldings	Polypropylene	Britain 1,403,797	1975	Imperial Chemical
General purpose	Ethylene-co-butadiene polymer (mostly <i>trans</i> -1,4-)	W. Germany 2,434,668	1975	Mitsui Petrochemical

Alt. styrene-co-maleic anhydride grafted—improved moldings	Polyethylene	Japan 2,167	1975	Mitsubishi Petrochemical
Adhesion promoter for polyolefin-polyamides	Propropylene	Japan 59,458	1975	Mitsubishi Rayon Co.
Polyamide-polyolefin moldings	Polypropylene	Japan 98,937	1975	Mitsubishi Petrochemical
Improved moldings	Polyethylene	Japan 44,863	1977	Sumitomo Chemical
Nylon-polyolefin composites	Polyethylene and polypropylene	Japan 85,242	1977	Mitsui Petrochemical
Thermositing composites	Polybutadienes	Japan 142,456	1978	Hitachi Cable
Film laminates	Ethylene propylene copolymer	Japan 82(3)	1979	Mitsubishi Chemical
Rubber composites with adhesion to metals	Liquid polyisoprene	United States 4,218,349	1980	Kuraray Co.
Metal-polyolefin composites	Polyethylene	Belgium 879,073	1980	Mitsui Petrochemical
Thermoplastic laminates	Tall oil pitch	Canada 1,075,390	1980	Northwood Mills Ltd.
Al foil-crystalline polymer laminates	Isotactic polypropylene	Japan 9,804	1980	Toyo Seikan Kaisha, Ltd.
Polyolefin-carbon fiber composites	Polyethylene, poly(butene-1)	Japan 50,041	1980	Toa Nenryo Kogyo
Floor-layer laminates	Ethylene-vinyl acetate copolymer	Japan 71,556	1980	Nippon Oil Co.
Olefin polymer laminates	Polypropylene	Japan 93,449	1980	Mitsui Toatsu Chemical
Chemical resistant laminates	Ethylene-1-butene copolymer	Europe 27,375	1981	Toa Chemical

OIL ADDITIVES

Lubricating oil	Butadiene-diisobutylene copolymers	United States 2,634,256	1953	Standard Oil
VI improvers	Polyisobutylene	Britain 852,949	1960	Esso Research
Fuels	Polyisobutylene	Britain 949,981	1964	Lubrizol Corp.
Fuels	Polyisobutylene	France 1,360,843	1964	Esso Research
Lubricants	Poly( $\alpha$ -olefins-co-nonconjugated diolefins)	France 1,396,598	1965	California Research
Lubricants	Ethylene-propylene rubber	Netherlands 2,968(69,70)	1965	Shell
Lubricants	Olefin-diolefin copolymers	United States 3,231,498	1966	Chevron Research
Lubricants	Polyalkenes	Britain 1,020,059	1966	Monsanto
Lubricants and fuels	Polyisobutylene	Netherlands 210	1966	Castrol Ltd.
Lubricants	Polyalkenes	Netherlands 8,794	1966	Castrol Ltd.



Table A.7 (cont.)

Applications	Substrate	Patent	Year	Assignee
Lubricants	Ethylene-propylene copolymer	United States 3,316,177	1967	Lubrizol Corp.
Fuels	Ethylene-co-propylene-co-dicyclopentadiene	United States 3,403,011	1968	Texaco
Fuels	Low mol. wt. polybutene	United States 3,447,918	1968	Standard Oil
Lubricants	Polyolefins	U.S.R. 259,307	1969	—
Fuels and lubricants	Polyisobutylene and poly(isobutylene-co-propylene)	South Africa 4,013	1969	Lubrizol Corp.
Lubricants	Polyolefins	United States 3,505,227	1970	Chevron Research
Lubricants	Polyisobutylene	United States 3,511,780	1970	Esso Research
Lubricants	Cracked ethylene-propylene-diene polymer	United States 3,513,095	1970	Texaco
Fuels	Poly(olefins-co-diolefins)	United States 3,523,768	1970	Chevron Research
Fuels	Poly( $\alpha$ -olefins)	United States 3,531,440	1970	Chevron Research
Fuels	Ethylene-propylene-diene terpolymer	United States 3,615,288	1971	Texaco
Fuels	Polyisobutylene	Britain 1,310,847	1971	Lubrizol Corp.
Lubricants	Polybutene	United States 3,647,692	1972	Standard Oil
Fuels	Olefin-diene copolymers and terpolymers	United States 3,652,239	1972	Texaco
Lubricants	Polyisobutylene	W. Germany 2,155,828	1972	Texaco
Lubricants	Polyisobutylene	United States 3,725,441	1973	Lubrizol Corp.
Lubricants	Polyisobutene	France 2,161,372	1973	Progil S.A.
Lubricants	Polybutenes	United States 3,855,251	1974	Standard Oil
Lubricants	Polyisobutylenes	Britain 1,356,802	1974	BP Chemicals
Lubricants	Polyalkenes	W. Germany 2,330,232	1974	Esso Research
Lubricants	Polybutenes	W. Germany 2,352,347	1974	Mobil Oil
Lubricants	Polyethylene	Japan 96,095	1974	Japan Oil Co.
Fuels	$\alpha$ -Olefin waxes	United States 3,909,215	1975	Chevron Research
Fuels	Low mol. wt. polyisobutylene	W. Germany 2,443,538	1975	Shell
Fuels and lubricants	Polyolefins	Japan 89,316	1975	Mitsubishi-Monsanto Chemical

Fuels	Polybutene	United States 3,935,249	1976	Standard Oil
Fuels	Low. mol. wt. polyisobutene	United States 3,997,569	1976	Texaco
Lubricants	Polyalkenes	Britain 1,483,729	1977	Shell
Lubricants	Polybutene	Japan 151,120	1977	Lubrizol Corp.
Lubricants	Atactic polypropylene	U.S.S.R. 564,309	1977	—
Viscosity index improvers	Hydrogenated styrene-butadiene copolymer	Belgium 859,662	1978	Shell
Lubricating oil	Ethylene copolymers	United States 4,137,185	1979	Exxon Research
VI improvers	Ethylene-co-propylene	Brazil 4,856	1979	Exxon Research
Lube oils	Ethylene-propylene-diene rubber	France 2,423,530	1979	Lubrizol Corp.
Lubricant compositions	Hydrogenated polybutadiene	Japan 20,008	1979	UBE Industries
Lube oils	Polyisobutylene	Europe 14,288	1980	Exxon Research
Fuel stabilizers	Polybutadiene	Japan 56,189	1980	Kao Soap Co.

PAPER MODIFIERS

Sizing agents	Petroleum resins	Japan 9,579	1963	High Polymer Chemical Ind.
Sizing agents	Petroleum hydrocarbon resins	Britain 986,616	1965	Sieko Chemical
Sizing agents	Petroleum resins	United States 3,279,975	1966	Yoshii, Ten
Sizing agents	Diene hydrocarbon resins	Britain 1,031,614	1966	Shell
Sizing agents	Petroleum resins	Britain 1,067,048	1967	Seiko Chemical
Sizing agents	Petroleum resins	Britain 1,090,604	1967	Mitsubishi Petrochemical
Coatings and sizing	Ethylene-co-propylene	France 1,516,761	1968	Hercules
Modifier for paperboard wax coatings	Low mol. wt. polyethylene	United States 3,428,591	1969	Atlantic Richfield
Paperboard wax coatings	Polyethylene	W. Germany 1,806,862	1969	Atlantic Richfield
Sizing agents	Petroleum resins	Japan 1,281	1970	Hamono Dye Works Co.
Sizing agents	Petroleum resins	Japan 5,723	1970	Kinkai Chemical Ind.
Sizing agents	Petroleum resins	Japan 14,123	1970	—
Sizing agents	Petroleum resins	Japan 28,722	1970	Kinkai Chemical Ind.
Sizing agents	Petroleum resins	Japan 32,762	1970	Kinkai Chemical Ind.
Sizing agents	Petroleum resins	Japan 39,041	1970	Hamano Dye Works
Sizing agents	Petroleum resins	Japan 39,481	1970	Hamano Dye Works
Sizing agents	Hydrocarbon resins	Japan 26,404	1971	Toho Chemical

Table A.7 (cont.)

Applications	Substrate	Patent	Year	Assignee
Sizing agents	Petroleum resins	Japan 40,883	1972	Seiko Chemical
Sizing agents	Polyolefins	Japan 33,994	1973	Research Institute Production Development
Sizing resins	Isobutylene-co-butadiene polymers	Japan 63,006	1973	Showa High-Polymer
Sizing agents	Terpene resins	Japan 6,121	1974	Toho Chemical
Sizing agents	Petroleum resins	Japan 21,245	1974	Kindai Chemical Ind.
Sizing agent	Hydrocarbon resins	W. Germany 2,434,216	1975	Nippon Oil
Synthetic paper	Polypropylene	W. Germany 2,458,822	1975	Mitsubishi Petrochemical
Sizing agents	Petroleum resin	Japan 9,881	1975	Gifu Ceramic
Synthetic paper	Polypropylene	Japan 90,644	1975	Mitsui Petrochemical
Sizing resins	Polyolefins	United States 4,071,581	1978	Nippon Oil
Sizing agents	Polyethylene	Japan 19,031	1978	Oji Paper
Sizing resins	Butadiene resins	Japan 42,405	1979	Nippon Oil
Paper size emulsions	Petroleum resins	Japan 25,444	1980	Kindai Chemical Co.

POLYMER ADDITIVES

Tackifiers	Unsaturated polyolefins	United States 2,555,595	1951	Shell
Extrusion aids	Polyethylene, polypropylene	United States 3,021,363	1965	Hercules
Polypropylene stabilizers	Polypropylene	Japan 16,395	1968	Mitsubishi Rayon
PVC modifier	Polyolefin waxes	France 2,009,350	1970	Farbwerke Hoechst
Esters as improved PVC modifiers	Polybutadiene	Japan 38,346	1971	Japan Oil
Modifier for polypropylene bottles	High mol. wt. polypropylene	Britain 1,335,791	1973	Mitsui Petrochemical
Modifier for polyolefin	Polypropylene	Japan 83,140	1973	Chisso Co.
Polyamide modifiers	Polyethylene	W. Germany 2,420,942	1974	Mitsui Petrochemicals
Alt. styrene-co-maleic anhydride grafted—polyamide lubricants	Polyethylene waxes	W. Germany 2,348,840	1975	BASF A.G.
Maleic anhydride-co-acrylic acid grafted coatings for polyolefin fillers	Poly(ethylene-co-vinyl acetate)	Japan 27,842	1975	Toyo Soda Mfg. Company



Tackifiers	Cyclopentadiene resins	W. Germany 2,856,335	1979	Mitsui Petrochemical
Thermal stabilizers	Polypropylene	Europe 28,085	1981	Toa Chemical
PLASTICS				
Polyolefins with improved impact	Polypropylene, polyethylene	France 2,132,780	1972	Esso Research
Nylon-polyolefin moldings	Polypropylene	W. Germany 2,145,408	1972	Mitsubishi Rayon
Molded ethylene-propylene rubber	$\alpha$ -Olefin polymers	United States 3,746,676	1973	Eastman Kodak
PVC-asbestos composites additive	Petroleum resins	Japan 54,157	1973	Mitsui Petrochemical
Moldings	Polyethylene	Japan 63,116	1973	Sumitomo Chemical
Rapid curing electrical molding composites	1,2-Polybutadiene	Japan 73,449	1973	Matsushita Electric
Surface grafted polyolefins	Polyolefin	Japan 78,244	1973	Showa Denko
Composites and moldings	Polypropylene	Japan 97,947	1973	Tokuyama Soda
Moldings	Polyethers	Britain 1,358,184	1974	Hercules
Reinforced moldings	Polypropylene	France 2,207,940	1974	Imperial Chemical
Injection moldings	Polypropylene	W. Germany 2,359,063	1974	Imperial Chemical
Thermoplastic-nitrile rubber poly-blends	Polypropylene	Japan 28,683	1974	Mitsui Petrochemical Ind.
Composites	Polypropylene	Japan 34,937	1974	Mitsubishi Petrochemical
Polyolefin cement composites	Polypropylene wax	Japan 36,748	1974	Tokuyama Soda
Polyolefin moldings	Polyolefins	Japan 41,096	1974	Mitsui Petrochemical Ind.
Molded articles	Ethylene-co-vinyl acetate	Japan 74,294	1974	Toyo Soda
Vinyl chloride-co-maleic anhydride graft—moldings	Vinyl acetate-co-ethylene polymer	Japan 75,686	1974	Toyo Soda
Injection moldings	Poly(phenylene ether)	Japan 112,953	1974	Asahi Dow
Moldings	Polypropylene	Japan 117,540	1974	Tokuyama Soda
Moldings with improved filler loadings	Polyethylene	United States 3,882,194	1975	Chemplex Co.
Polyamide-polyolefin moldings	Polypropylene	Britain 1,403,797	1975	Imperial Chemical
Composites	Dicyclopentadiene resins	W. Germany 2,358,722	1975	Hoechst A.G.
Alt. styrene-co-maleic anhydride grafted—improved moldings	Polyethylene	Japan 2,167	1975	Mitsubishi Petrochemical

Table A.7 (cont.)

Applications	Substrate	Patent	Year	Assignee
Hot melt	HD Polyethylene	Japan 4,144	1975	Mitsui Petrochemical Ind.
Polyolefin adhesion promoter for laminates	Polypropylene	Japan 4,167	1975	Mitsubishi Petrochemical
Moldings	Polypropylene	Japan 61,469	1975	Mitsubishi Petrochemical
Containers and moldings	Polyolefins	Japan 86,578	1975	Denki Kagaku Kogyo
Polyolefins—polyamides moldings	Polyethylene	Japan 87,178	1975	Mitsui Petrochemical Ind.
Polyamide—polyolefin moldings	Polypropylene	Japan 98,937	1975	Mitsubishi Petrochemical
Improved moldings	EPDM rubber	W. Germany 2,644,492	1977	Anic S.p.A.
Molding resins	Polyolefins	Japan 30,546	1977	Mitsui Petrochemical Ind.
Improved moldings	Polyethylene	Japan 44,863	1977	Sumitomo Chem.
Grafting on moldings to improve stability	Polyolefin moldings	Japan 58,772	1977	Toyo Spinning
High strength molding resins	HD Polyethylene	United States 4,071,494	1978	Champion Int. Corp.
Maleic anhydride copolymer fire retardants	Epichlorohydrin polymer (Hydrin 100)	United States 4,108,943	1978	Monsanto
Blood compatible thermoplastics	Polyolefins	Belgium 868,208	1978	Hoechst A.G.
Heat- and shock-resistant moldings	Ethylene—propylene—diene ter-polymer	W. Germany 2,644,492	1978	ANIC S.p.A.
Grafting procedures	Poly(vinyl chloride) dehydrohalogenated	Japan 22,588	1978	Osaka Soda
Thermosetting composites	Polybutadienes	Japan 142,456	1978	Hitachi Cable
Fiber glass laminates	Poly(1,2-butadiene)	Japan 149,285	1978	Fujitsu Ltd.
Extrusions and moldings	Ethylene—vinyl acetate copolymer	United States 4,157,362	1979	Toyo Soda
Polyolefins with improved dyeability	Polypropylene	W. Germany 2,708,757	1979	Idemitsu Ind.
Polyolefin laminates	Polypropylene	Japan 41,972	1979	Mitsubishi Petrochemical
Heat-resistant moldings	Polyolefins	Japan 53,158	1979	Mitsui Petrochemical
Laminates	Ethylene—vinyl acetate copolymer	Japan 110,282	1979	Nippon Petrochemical
Resin compositions for laminates	Liquid conj. diolefin polymers	Japan 145,789	1979	Sumitomo Chemical
Laminated plastic containers	Polyethylene	Japan 152,087	1979	Toppan Printing Co.
Glass-fiber filled laminates	Butadiene polymers and copolymers	Poland 98,524	1979	Politechvika Wroclawska

Polyolefin-based electric-insulating compositions	Carbon black	U.S.S.R. 697,533	1979	—
Plastics with good coating, adhesion and plating properties	Polypropylene	United States 4,181,689	1980	Idemitsu Kosan Co.*
Molding resins	Butadiene or isoprene polymers	United States 4,197,263	1980	Standard Oil
PPO composites of styrene-MA graft materials	Polybutadiene	United States 4,221,880	1980	ARCO Polymers
Rubber modified molding resins	Butadiene rubber	Europe 9,529	1980	Monsanto
Plastics with improved melt flow properties	Styrene-diene block copolymers	W. Germany 2,943,657	1980	Asahi Chemical
Laminated plastic materials	Butadiene-styrene block copolymer	W. Germany 2,952,359	1980	Asahi Chemical
Modifier for cold stampable poly-blends	Polybutadiene	W. Germany 3,005,175	1980	Nippon Oil Co.
Laminates	Polyethylene	W. Germany 3,008,749	1980	Asahi Chemical
Thermoplastic polyester polyblends	Poly(butylene) ethylene-1-butene copolymer	Japan 21,430	1980	Mitsubishi Chemical
Polyolefins with improved impact properties	Polyethylene	Japan 31,860	1980	Adeka-Argus Ind.
Polyamide-polyolefin blends	Ethylene-propylene copolymer	Japan 36,279	1980	Mitsubishi Chemical
Moldings with improved modulus and heat distortion	Polypropylene	Japan 50,040	1980	Idemitsu Kosan Co.
Multilayer containers	Polypropylene	Japan 71,241	1980	Toppan Printing Co.
Blow molding containers	Polyolefins	Japan 71,242	1980	Sekisui Chemicals Ind.
Polyolefin composites	Polybutadiene	Japan 112,248	1980	Furukawa Electric
Thermoplastic elastomers	$\alpha$ -Olefin polymers	Netherlands 503	1980	Stamicarbon BV
Crosslinked, molded sheets	Polyethylene	Romania 64,350	1980	Combinatul Petrochimic

PRINTING INKS

Modified resins	Polyethylene, polypropylene, and polystyrene	United States 3,216,885	1965	Union Carbide
Inks and floor polishes	Hydrocarbon waxes	Britain 1,182,161	1970	Petrolite Corp.
General purpose	Butadiene-co-cyclopentadiene polymer	Britain 1,356,309	1974	Esso Research



Table A.7 (cont.)

Applications	Substrate	Patent	Year	Assignee
Ink resins	Hydrocarbon resins	W. Germany 2,264,284	1974	Reichhold-Albert
Ink resins	Petroleum resins	W. Germany 2,418,520	1974	Nippon Oil
Gravure printing	Petroleum resins	Japan 118,503	1974	Mitsui Petrochemical Ind.
Styrene-co-maleic anhydride grafted	Cyclopentadiene resins	W. Germany 2,347,813	1975	Hoechst A.G.
Styrene-co-maleic anhydride grafted	Hydrocarbon resins	W. Germany 2,347,843	1975	Hoechst A.G.
Ink resins	Petroleum resins	W. Germany 2,442,526	1975	Imperial Chem.
Air dry and printing inks	Liquid <i>cis</i> -1,4-polybutadiene	W. Germany 2,604,680	1976	Sumitomo Chem.
Printing ink binders	Cyclopentadiene resins	Belgium 849,659	1977	AKZO N.V.
Floor polishes and ink resins	Polyolefin waxes	W. Germany 2,710,025	1977	Nippon Oil
Ink resins	Cyclopentadiene resins	Japan 12,232	1977	Hoechst A.G.
Binder for inks	<i>cis</i> -1,4-Polybutadiene	United States 4,105,610	1978	Hoechst A.G.
Ink binders	Cyclopentadiene resin	W. Germany 2,815,092	1978	Nippon Zeon
Ink compositions	Hydrocarbon resins	United States 4,169,821	1979	Hoechst A.G.
Ink resins	Cyclopentadiene resins	United States 4,183,833	1980	Nippon Zeon Co.
Ink resins	Methyl dicyclopentadiene resins	United States 4,189,410	1980	Neville Chemical Co.
Emulsion lithographic inks	Petroleum resins	Japan 5,946	1980	Toyo Ink
Ink binder resins	Poly(cyclopentadiene)	Japan 50,004	1980	Nippon Zeon
SURFACE ACTIVE AGENTS				
Surface active agents	Polyolefins	United States 2,514,533	1950	Universal Oil
Hydrophilic high polymers	Diolefin copolymers	Japan 83,091	1979	Dainichi Seika Kogyo
Polyolefin surface treatment agent	Ethylene-propylene copolymer	Europe 9,971	1980	Mitsui Petrochemical Ind.
SOIL ADDITIVES				
Stabilizers	Polybutadiene	Netherlands 10,628	1965	Badische Anilin

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## CHAPTER 4

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## CHAPTER 5

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## CHAPTER 8

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## CHAPTER 10

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## CHAPTER 11

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## CHAPTER 12

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